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HYDROCARBON FUEL CELL ELECTRODES

Progress Report No. 6

July 16, 1967 - January 15, 1968

Prepared for

U. S. ARMY MOBILITY EQUIPMENT RESEARCH AND DEVELOPMENT CENTER

FORT BELVOIR, VIRGINIA

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FOREWORD

This is Interim Progress Report No. 6 of a research program on fuel cell electrodes conducted by the Central Research Division of American Cyanamid Company under contract with the U. S. Army Mobility Equipment Research and Development Center.

The principal objective of the program is to obtain 0.75 volt at current densities of 100 amperes per square foot, in matrix cells operating with phosphoric acid electrolyte at 100-150°C and utilizing hydrogen containing 3-5 mole % carbon monoxide.

During the present report period, manpower levels were increased. The expanded effort placed greater emphasis on anode catalyst evaluation, and included development and evaluation of improved matrix materials, in addition to life-testing with standard and experimental components.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

(Continued)

Glossary of Terms

Electrodes

AA - Unsupported noble metal catalyst applied with PTFE to a tantalum screen.
 AA-1 9 to 10 mg Pt/cm² on 50 mesh tantalum screen.
 AA-2 9 to 10 mg Pt/cm² on expanded tantalum screen.
 AA-3 5 mg Pt/cm² on 50 mesh tantalum screen.

BA - Noble metal(s) deposited on or mechanically mixed with a substrate material and applied with PTFE to a tantalum screen.

RA - CO resistant anode. 42.5/42.5/15 weight ratio $Pt/Rh/WO_2$ catalyst (mechanically mixed with Cyanamid Graphite at low loadings) applied with PTFE to an expanded tantalum screen:

Loading, mg/cm²

	Pt	Rh	WO₂	Graphite
RA-1	7.5	7.5	2.6	0.0
RA-2	2.5	2.5	0.9	4.1
RA-3	1.5	1.5	0.5	6.5

Matrices

TA - A highly porous matrix consisting of wettable corrosion resistant filler materials bound by PTFE.
 TA-1 Etched PTFE floc filler.
 TA-2 Zirconium pyrophosphate filler.

Electrode Backing

L Type - a pliable micro-porous PTFE film which forms a gas permeable - liquid impermeable barrier.

1. SUMMARY

1.1 Evaluation of General Electric Company Catalysts and Electrodes

Several samples of anode catalysts comprising platinum codeposited with other noble metals (principally ruthenium) on boron carbide or a boron carbide-mixed chromium-tungsten oxide substrate were obtained from General Electric Company. These catalysts were made into electrodes and tested in matrix cells in 5 $\underline{N}$ H_2SO_4 (70°C, 1% CO) and 95-97% H_3PO_4 (150°C, 10% CO). Data were also obtained for several electrodes prepared by General Electric Company from one of the above catalysts.

Electrodes prepared from these catalysts using American Cyanamid Company's standard fabrication techniques gave results that were generally somewhat poorer than were obtained with equivalent loadings of type RA catalysts. Significant improvements were observed in some cases when graphite was added to the catalysts, and one sample, with added graphite and a heat-treatment, gave outstanding results. The electrodes prepared by General Electric Company gave good initial performance. Further work will be done to modify our electrode fabrication techniques to accommodate boron carbide-based catalysts.

1.2 Electro-Catalysis Studies: Sulfur-Covered Platinum Black Electrodes

The effect of adsorbed surfur on the current-potential behavior of platinum black electrodes operating on impure hydrogen in phosphoric acid electrolyte was examined. The stability of the sulfur-covered platinum surface with time was also briefly investigated.

Sulfur was deposited on the platinum black surface by addition of sodium sulfide to a sulfuric acid solution in which the electrode was immersed. Cyclic voltammetric techniques were used to

estimate the amount of sulfur on the surface, and to study the effects of the adsorbed sulfur on the combined hydrogen-carbon monoxide electrode process.

Polarization data were obtained in a free electrolyte cell operating with 95-97% phosphoric acid at 100°C, using impure hydrogen fuel mixtures containing 1-10% CO. With sulfur-covered type AA electrodes at 5 and 10 mg Pt/cm^2, significant decreases in polarization as compared with the same electrodes without sulfur were observed. However, these improvements do not appear to be as great as can be obtained by other means, such as the use of type RA catalysts.

Cyclic voltammetric measurements indicate that at least over short periods (up to 18 hours), the sulfur-covered platinum surface is stable in phosphoric acid at 100°C so long as the electrode potential is maintained below the oxidation potential of sulfur (approximately 0.7 V with respect to a hydrogen reference electrode in the same electrolyte).

1.3 Matrix Development and Evaluation

Work in this area included corrosion testing of various possible filler materials, and the preparation and evaluation of experimental matrices. The matrices were characterized in terms of their dimensional stability, porosity, bubble pressure, and resistivity.

Corrosion tests at 150 and 200°C in 100% phosphoric acid were run on various forms (fiber and powders) of fused quartz, tantalum pentoxide, and zirconium pyrophosphate. Of these materials, tantalum pentoxide powder showed the greatest stability (1% weight loss at 150°C, 11% at 200°C). With commercial tantalum pentoxide fiber and cloth samples,

on the other hand, weight loss was significant at 150°C and severe at
200°C. Zirconium pyrophosphate also was significantly attacked at both
temperatures. Fused quartz showed little weight loss at higher tempera-
ture, but microscopic examination showed evidence of severe structural
degradation.

The dimensional stability of matrices prepared with
etched PTFE (TA-1), zirconium pyrophosphate (TA-2) and fused quartz
fillers when exposed to hot phosphoric acid was investigated. These
matrices as manufactured are in a water-wet condition, and in normal
handling are equilibrated directly in the phosphoric acid electrolyte.
For matrices handled in this way, dimensional stability in hot phosphoric
acid was poor (area losses of 16-57% and thickening of 44-92% were observed
after 300 hours' exposure to 100% H_3PO_4 at 150°C and 200°C). It was found,
however, that if the matrices are dried prior to equilibration with phos-
phoric acid, dimensional stability is greatly improved. In the drying
process, some loss in porosity is incurred.

The effect of heat-treating the dried matrices was studied.
Heat-treating at 250-300°C (below the sintering temperature of PTFE) had
little effect on dimensional stability, but may have improved the
rewettability of some of the materials. Heating at 340-360°C caused
severe shrinkage with the TA-1 matrix, and drastic loss of mechanical
strength with most of the other materials.

1.4 Life Testing

Major emphasis during this period was placed on determining
the performance levels and stability which may be expected from standard
electrode-matrix combinations operating at 100 mA/cm² on impure H_2 fuel

with phosphoric acid electrolyte at 100-150°C. A limited amount of evaluation work was also done with experimental anode and cathode structures.

Several life tests using the standard TA-1 matrix and operating on pure hydrogen fuel have been run for periods longer than 7,000 hours. Overall decline rate for the 7,000-hour period was 1.5-3 mV/100 hours in two tests at 150°C, and less than 1 mV/100 hours in one test at 100°C. Initial voltage was 0.69-0.71 volt for the 150°C tests, and 0.66 volts for the 100°C test.

A number of impure hydrogen fuel mixtures have been used in the life testing program. Early work was carried out with binary mixtures containing up to 10% CO in hydrogen. More recently, a synthetic reformate (3% CO, 27% CO_2, 70% H_2 for tests at 150°C and 1% CO, 29% CO_2, 70% H_2 for tests at 100°C) has been used. The stability of the RA-2 anode on impure hydrogen fuel at 150°C has been evaluated in several ways. In tests which were alternated periodically between pure hydrogen and hydrogen containing 10% CO, the voltage loss (from pure to impure hydrogen) appeared to increase somewhat with time. Also, in tests run for longer periods on 10% CO in hydrogen and on the synthetic reformate, the voltage decline rates appeared to be somewhat higher than in corresponding tests with pure hydrogen. On the other hand, reference electrode measurements made in several tests of up to 1,400 hours' duration indicated that the anode was relatively stable, while the cathode declined nearly linearly with time. Overall, the major stability problem with respect to operation at temperatures of 150°C or higher appears to lie with the cathode.

Two apparently significant factors affecting the performance of RA-2 anodes at 150°C were noted: (1) the use of a secondary extractable filler in the electrode preparation to modify the pore structure, and (2) oxygen treatment of the anode during start-up. Based on limited data, both of these procedures appeared to improve performance stability on synthetic reformate. Further work is needed to confirm and to optimize these effects.

Best performance to date with synthetic reformate at 150°C has been achieved with RA-2 electrodes having the modified pore structure. In several tests, peak voltages of 0.70-0.71 V at 100 mA/cm^2 were obtained, with voltage decline rates over the first 1,000 hours of approximately 7 mV/100 hours.

Type BA (platinum on graphite) cathodes at 5-10 mg Pt/cm^2 were evaluated in a number of life tests. Performance was quite variable from test to test, and generally lower than that for AA-2 cathodes, but there is some evidence that this type of cathode may operate more stably.

Testing at 100°C was generally hampered by poor reproducibility. Best performance with RA-2 anodes on pure hydrogen was in the range 0.64-0.66 V at 100 mA/cm^2, and on synthetic reformate (1% CO), approximately 0.60 V.

2. INTRODUCTION

While the original objectives of the work being carried out under this contract involved direct hydrocarbon conversion in matrix type fuel cells, recent emphasis has been placed on development of an effective electrode-matrix combination for utilization of impure hydrogen fuel obtained by reforming of hydrocarbons. During the period covered by Report No. 5 (January, 1967 - July, 1967), work was carried out in both sulphuric and phosphoric acid electrolyte systems. In view of the generally poor results obtained with sulfuric acid, however, life testing during the present period was done only with phosphoric acid electrolyte. Emphasis was placed on characterizing the performance of standard RA-2 anodes and AA-2 cathodes on synthetic reformer gases containing 1-3% carbon monoxide and 70% hydrogen (balance carbon dioxide).

Because it was felt that more effective anode catalysts and cathode structures would be required to reach the stated objective of 0.75 V at current densities in excess of 100 amperes/ft^2, work in the catalyst area has been increased. Also, in order to take advantage of the increased tolerance of anode catalysts toward carbon monoxide and the increased reactivity of hydrocarbons at temperatures up to 200°C, the need was felt for a matrix compatible with strong phosphoric acid electrolyte in this temperature range. Accordingly, the contract effort was expanded to include matrix development and evaluation. The present report describes the progress made in these various areas during the period July, 1967 to January, 1968.

3. RESULTS AND DISCUSSION

3.1 Evaluation of General Electric Company Catalysts and Electrodes

During the latter part of this report period work was initiated under this contract to cover several aspects of catalysis as it pertains to matrix cell testing on carbon monoxide mixtures in hydrogen. This section and the one that follows report two directions in which work has progressed.

A number of promising catalysts for hydrogen/CO mixtures have been developed by General Electric Company under contract to MERDC.[14] These catalysts were developed for, and had been tested primarily in, sulfuric acid free-electrolyte cells. Preliminary evaluation by American Cyanamid Company of several of these catalysts in the phosphoric acid matrix system is reported here.

The catalysts obtained from General Electric Company are listed in Table 3.1-1. There were two types, one consisting of various noble metal mixtures supported (at 10-20% noble metal) on a boron carbide base, and the other consisting of 16.7% (Pt-Ru 7:3) on a mixed base ($B_4C + Cr_2O_3 \cdot WO_x$ in varying proportions). Three electrode sheets prepared by General Electric Company from catalysts of the latter type were also submitted for our evaluation.

3.1.1 Apparatus and Techniques

The apparatus and the experimental techniques used for this work were similar to those used in the life testing program. The cell design was similar to that described in Progress Report No. 1[1a] except adapted to use a one-inch diameter electrode disc (5 cm^2 active area). Cell parts were of solid tantalum metal and platinum mesh spacer screens were used along with PTFE gaskets and glass fiber paper as a matrix material. Internal cell resistances under open circuit conditions

Table 3.1-1

Catalysts Received from General Electric Company

Identification	Composition	Support	Crystallite Size[1] A°
8462-150-1	10% (Pt-Ir 4:1)	B_4C	50
8728-20-1	10% (Pt-Rh 1:1)	B_4C	50
8728-20-4	10% (Pt-Ru 4:1)	B_4C	20
8728-39-3	20% (Pt-Ru 1:1)	B_4C	15
8728-42-1	20% (Pt-Rh 1:1)	B_4C	20
8821-115A[2]	20% Pt	B_4C	60
8821-115B[2]	20% (Pt-Ru 3:2)	B_4C	25
8808-141A	16.7% (Pt-Ru 7:3)	$B_4C + Cr_2O_3 \cdot WO_x$, 1:1	-
8808-141B	16.7% (Pt-Ru 7:3)	$B_4C + Cr_2O_3 \cdot WO_x$, 1:2	-
8808-141C	16.7% (Pt-Ru 7:3)	$B_4C + Cr_2O_3 \cdot WO_x$, 1:3	-

[1] Measured in Cyanamid Laboratories by X-ray line broadening for the noble metals present.

[2] 10 gram samples. All other samples were approximately 2 grams.

were measured with a Keithley Model 503 line-operated milliohmmeter before and after the polarization curve. At each point of the polarization curve, the current density was maintained for at least two minutes. Normally, data were obtained in 5 $\underline{N}$ H_2SO_4 at 70°C and in 95-97% H_3PO_4 at 150°C.

The catalyst powders received from GE were formed into electrodes by our usual laboratory procedure. A mixture of the catalyst, Baymal alumina filler and PTFE latex (du Pont 30B), was spread on a 2" x 2" tantalum screen, dried and then washed with trichloroethylene, ethanol, and finally hot 5 $\underline{N}$ H_2SO_4 to remove the alumina filler. The percentage of PTFE used was 14%. Using a normal catalyst loading of 10 mg/cm^2 gave 1-2 mg noble metal/cm^2 depending on the percentage of noble metal in the catalyst.

Where graphite was added, it was usually done at 50% of the weight of the catalyst used, and the PTFE was increased correspondingly to keep the same 14% in the final electrode. In several tests, a heat treatment was applied to the formed electrode by placing it in a Carver press at contact pressure for five minutes at 280°C. In these heat treated samples, the PTFE level was lowered to 10%.

Since the catalysts discussed in this section were designed for use as anodes, all cells were assembled with a counter-electrode (cathode) which was a standard AA-1 electrode with 9 mg Pt/cm^2, operating on oxygen.

3.1.2 Catalysts Supported on Boron Carbide

The results obtained in H_2SO_4 at 70°C with the boron carbide-based electrodes are summarized in Table 3.1-2. In general, most of the results on hydrogen were low compared to graphite-based

Table 5.1-2

Performance of GE Boron Carbide-Based Anode Catalysts

70°C, 5N H_2SO_4, Glass Fiber Matrix

AA-1 Cathode on Oxygen

Catalyst	Noble Metal Loading (mg/cm²)	Performance on H_2 (volts at indicated current density)				Performance on 1% CO/H_2 (volts at indicated current density)			
		40	100	200	400 mA/cm²	40	100	200	400 mA/cm²
A Catalyst as received									
8462-150-1	0.8 Pt + 0.2 Ir	.81	.67	-	-				
8728-20-1	0.5 Pt + 0.5 Rh	.83	.76	.64	-				
8728-20-4	0.8 Pt + 0.2 Ru	.82	.74	.60	-				
8728-39-3	1.0 Pt + 1.0 Ru	.84	.78	.71	.54	.78	.44	-	-
8821-115A	2.0 Pt	.87	.83	.78	.69	-	-	-	-
8821-115B	1.2 Pt + 0.8 Ru	.86	.81	.76	.68	.81	.60	.39	.15
8821-115B*	1.2 Pt + 0.8 Ru	.83	.78	.73	.63	.70	.42	.27	-
B Catalyst with added graphite									
8728-20-1	0.5 Pt + 0.5 Rh	.85	.81	.77	.70	.51	.35	-	-
8728-39-3	1.0 Pt + 1.0 Ru	.84	.79	.74	.66	.81	.66	-	-
8821-115B	1.2 Pt + 0.8 Ru	.75	.70	.64	.56	.71	.47	.29	-
8821-115B*	1.2 Pt + 0.8 Ru	.87	.84	.79	.74	.83	.66	.40	.22
C Cyanamid Catalysts for comparison									
BA-2A	1.0 Pt	.88	.84	.80	.75				
RA	0.5 Pt + 0.5 Rh	-	-	.80	-	.72	.32	-	-
RA	1.0 Pt + 1.0 Rh	.88	.84	.80	.73	.77	.50	-	-

* Electrode heated 5 minutes at 280°C

catalysts although the more recent catalyst (8821-115B) did perform
well, especially on graphite addition and heat treatment. On carbon
monoxide (1% CO in H_2) the performance of several samples was very good.
In some cases graphite addition materially helped the performance results.
The earlier samples without added graphite had abnormally high internal
cell resistance (2 to 5 times the normal value of 0.03 to 0.05 ohms for
a 5 cm^2 cell).

Similar data are shown in Table 3.1-3 for tests at 150°C
in H_3PO_4. Again, most results on hydrogen were low compared with graphite-
based catalysts. One electrode made from catalyst 8821-115B was excep-
tionally good, however, both on hydrogen and 10% CO in hydrogen. This
electrode contained added graphite, and had been heat-treated for five
minutes at 280°C. A repeat test on this same electrode confirmed the
results shown in Table 3.1-3. However, three later attempts to reproduce
this electrode, using the same catalyst batch, resulted in lower performance.

It is interesting to note that for catalyst 8821-115B,
tested in sulfuric acid, neither graphite addition alone nor heat-treatment
alone improved performance as compared with the "as received" catalyst.
In phosphoric acid, addition of graphite alone was not helpful, but the
heat-treatment improved performance with or without graphite addition.
Obviously, further work is needed to optimize the processing variables
for maximum performance. In particular, the inter-relationships between
catalyst, substrate, PTFE level, and conditions of heat-treatment need to
be studied.

Table 3.1.3

Performance of GE Boron Carbide Based Anode Catalysts

150°C, 85% H_3PO_4, Glass Fiber Matrix, AA-1 Cathode on Oxygen

Catalyst	Noble Metal Loading mg/cm²	Performance on H_2 Volts at indicated current density				Performance on 10% CO/H_2 Volts at indicated current density			
		40	100	200	400 ma/cm²	40	100	200	400 ma/cm²
A. Catalyst as received									
8728-42-1	1.0 Pt + 1.0 Rh	.87	.81	.72	.59	.84	.68	.29	-
8728-39-3	1.0 Pt + 1.0 Ru	.85	.76	.53	-	.83	.53	-	-
8821-115A	2.0 Pt	.89	.83	.74	.56	-	-	-	-
8821-115B	1.2 Pt + 0.8 Ru	.86	.79	.72	.54	.84	.70	.35	-
8821-115B*	1.2 Pt + 0.8 Ru*	.89	.83	.75	.63	.87	.77	.51	.31
B. Catalyst with added graphite									
8728-20-1	.5 Pt + .5 Rh	.88	.82	.73	.57	.85	.60	-	-
8728-36-3	1.0 Pt + 1.0 Ru	.86	.80	.72	.60	.85	.76	.53	-
8821-115B	1.2 Pt + 0.8 Ru	.87	.80	.70	-	.70	-	-	-
8821-115B*	1.2 Pt + 0.8 Ru	.90	.85	.79	.72	.90	.83	.75	.62
C. Cyanamid Catalysts for Comparison									
PA-2A	1.0 Pt	.90	.85	.79	.69	-	-	-	-
PA	0.5 Pt + 0.5 Rh	.90	.85	.78	.67	.87	.77	.47	-
PA	1.0 Pt + 1.0 Ph	.90	.84	.77	.67	.89	.80	.64	-

* Electrode heated 5 minutes at 280°C

3.1.3 Catalysts Supported on Mixed Oxides

Three samples were obtained from General Electric Company of 16.7% platinum-ruthenium on a mixed base of B_4C and $Cr_2O_3-WO_x$ in several ratios. The catalysts as received were in the unreduced form (preferred by GE for best results) so that modifications in the electrode preparation were necessary to avoid dissolving the metal salts during the acid washing step. The electrodes prepared from these catalysts did not give good results in H_2SO_4 or in H_3PO_4, although a heat treatment did give some improvement. Following discussions with GE personnel, several electrodes prepared in the General Electric Laboratories were submitted for our evaluation.

3.1.4 Electrodes from General Electric Company

Three electrode discs were received from General Electric Company. One of these had an applied PTFE backing and has not been tested as yet. The other two electrodes contained 5 mg noble metal/cm^2 on a platinum screen with 8% PTFE binder-waterproofing agent and with no applied backing. These electrodes were tested in the matrix cell at 70°C in H_2SO_4, with the results shown in Table 3.1-4. Both GE electrodes (1176 and 1174) gave rather low performance on hydrogen (40-50 mV below RA-2 at 100 mA/cm^2), but the drop in going from pure hydrogen to 1% CO in hydrogen was about the same as for RA-2 electrodes.

The results in H_3PO_4 at 150°C are shown in Table 3.1-5. Here the GE electrodes performed very well both on hydrogen and on 10% CO and were comparable to the RA-2 electrode. It is apparent that the GE catalysts can give very good performance at 150°C in phosphoric acid matrix cells. It seems desirable to run life tests on electrodes similar

Table 3.1-4

Performance of General Electric Electrodes (Anodes)

Catalyst: Noble Metal Supported on $B_4C/Cr_2O_3-VO_x$

Metrix Cell - Glass Fiber

70°C H_2SO_4

AA-1 Cathode on Oxygen in all Cells

Fuel	Electrode #	Noble Metal mg/cm^2	Performance - Volts at				
			40	100	200	400	600 mA/cm²
H_2	AA-1	9.0 Pt	.88	.85	.82	.78	.74
H_2	BA-2A[1]	1.0 Pt	.88	.84	.80	.75	.70
H_2	1176[2]	3.5 Pt + 1.5 Ru	.82	.77	.73	.65	.58
H_2	1174[2]	3.5 Pt + 1.5 Ru	.83	.78	.73	.66	.59
H_2	RA-2[1]	2.5 Pt + 2.5 Rh	.86	.82	.78	.70	.64
1% CO	1176[2]	3.5 Pt + 1.5 Ru	.77	.70	.59	--	--
1% CO	1174[2]	3.5 Pt + 1.5 Ru	.80	.73	.62	--	--
1% CO	RA-2[1]	2.5 Pt + 2.5 Rh	.84	.77	.64	--	--

(1) contains graphite

(2) G. E. electrode

Table 3.1-5

Performance of General Electric Electrodes (Anodes)

Catalyst: Noble Metal Supported on $B_4C/Cr_2O_3-WO_x$

Matrix Cell - Glass Fiber

150°C H_3PO_4

AA-1 Cathode on Oxygen in all Cells

Fuel	Electrode #	Noble Metal mg/cm²	Performance - Volts at				
			40	100	200	400	600 mA/cm²
H_2	AA-1	9.0 Pt	.89	.84	.73	.69	.62
H_2	BA-2A[1]	1.0 Pt	.90	.85	.79	.69	.60
H_2	1176[2]	3.5 Pt + 1.5 Ru	.82	.78	.73	.67	.61
H_2	1174[2]	3.5 Pt + 1.5 Ru	.87	.82	.76	.63	.60
H_2	RA-2[1]	2.5 Pt + 2.5 Rh	.86	.81	.76	.68	.62
10% CO	1176[2]	3.5 Pt + 1.5 Ru	.84	.78	.72	.59	--
10% CO	1174[2]	3.5 Pt + 1.5 Ru	.87	.81	.73	.60	--
10% CO	RA-2[1]	2.5 Pt + 2.5 Rh	.87	.81	.74	.62	--

(1) contains graphite

(2) G. E. electrode

to these, and to put further effort into forming GE catalysts into electrodes by modification of our electrode processing variables.

3.2 Electrocatalysis Studies: Sulfur-Covered Platinum Black Electrodes

Binder et al[3-6] have shown that the oxidation of carbon monoxide in sulfur acid proceeds much more easily on a sulfur-covered platinum surface than on pure platinum. In the present study, this idea has been extended to phosphoric acid electrolyte at higher temperatures and to mixtures of carbon monoxide in hydrogen, using lower amounts of platinum metal. The stability of the sulfur-covered platinum surface was also investigated.

3.2.1 Apparatus and Techniques

The electrolysis cell and reference electrode assemblies used in these studies, together with electrical connections to the potentiostat, function generator, and X-Y recorder, are shown in Figure 3.2-1. The working and the auxiliary electrodes were accommodated in a conventional H-type Pyrex electrolysis cell. Each compartment had a sintered glass disc through which nitrogen was continuously bubbled. Both compartments were covered by PTFE stoppers having the required number of holes for the electrode holders, reference probe, and other equipment. Each compartment could also be fitted with a water condenser, if desired, to keep the electrolyte concentration constant. The cell was maintained at constant temperature by means of an oil bath.

The auxiliary electrode assembly used an 80-mesh Pt gauze or a Pt black (AA-2) electrode. The use of a sintered glass disc as well as continuous bubbling of nitrogen prevented the gases evolved at

ELECTROLYSIS CELL AND AUXILIARY EQUIPMENT
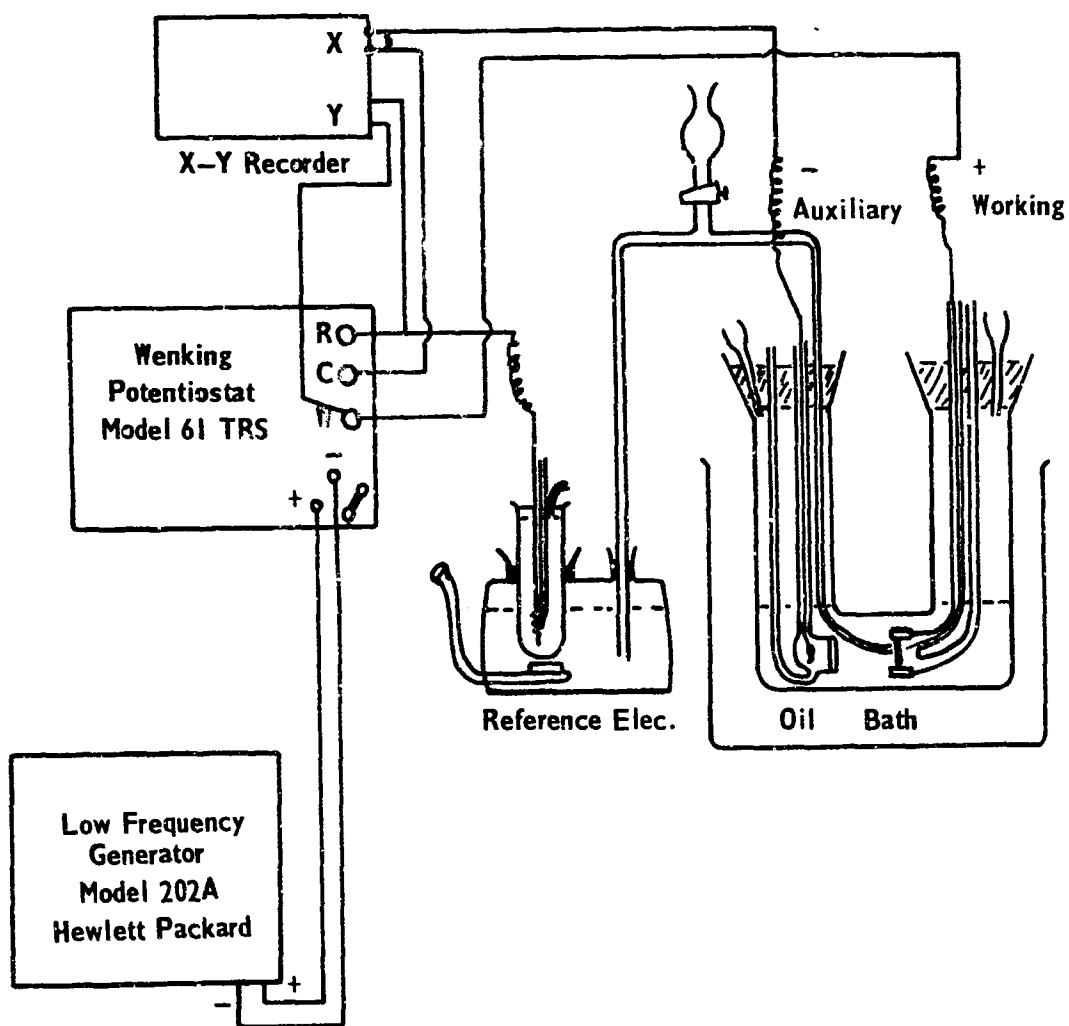
FIGURE 3.2-1

the cathode from reaching the anode. The auxiliary electrode, if desired, could be very easily replaced by an oxygen or air depolarized cathode as used in a free electrolyte fuel cell.

Anode potentials were measured with respect to a hydrogen reference electrode, at room temperature, using the same electrolyte as in the test cell. Connection to the test cell was made through a bridge and Luggin capillary, as shown in Figure 3.2-1. The hydrogen reference electrode was constructed from PTFE-bonded platinum black on platinum screen. Hydrogen was bubbled over the electrode, which was isolated from the main body of the solution by a Vycor tube and porous Vycor bulb.

Test Electrodes

Cyanamid Type AA-1, AA-2, and AA-3 electrodes (see Glossary) have been investigated so far in these studies. These electrodes were made liquid impermeable by application of a porous polyfluorocarbon backing material (Cyanamid L-3 backing). The backing was applied to 1-3/8 inch diameter electrode discs by pressing at 150 psi and 150°C for 5 minutes. Connection to the fluorocarbon-backed anode (test electrode) was made by a platinum wire spot-welded to the tantalum screen. In the anode half-cell, shown in Figure 3.2-2, the area of the electrode exposed to the electrolyte was 5 cm^2. Advantages of this electrode assembly include ease of changing the electrodes, and of keeping any desired gas atmosphere at the back of the electrode.

Cyclic Voltammetry and Polarization Curves

A Hewlett-Packard Model 202A Low Frequency Generator was used to drive the Wenking Potentiostat, Model 61TRS. The potentiostat was connected to the respective electrodes as shown in Figure 3.2-1, and the data were recorded on a Moseley Model 135 X-Y recorder.

ANODE HALF-CELL

THERMOSTATTED
ELECTROLYTE

Key:
A   Anode connection
B   Gas inlet
C   Glass electrode holder
D   Threaded PTFE cap
E   Anode face (1-in. diam.)
F   Capillary (out of proportion)
G   Product gas outlet
H   Bridge to hydrogen
    reference electrode
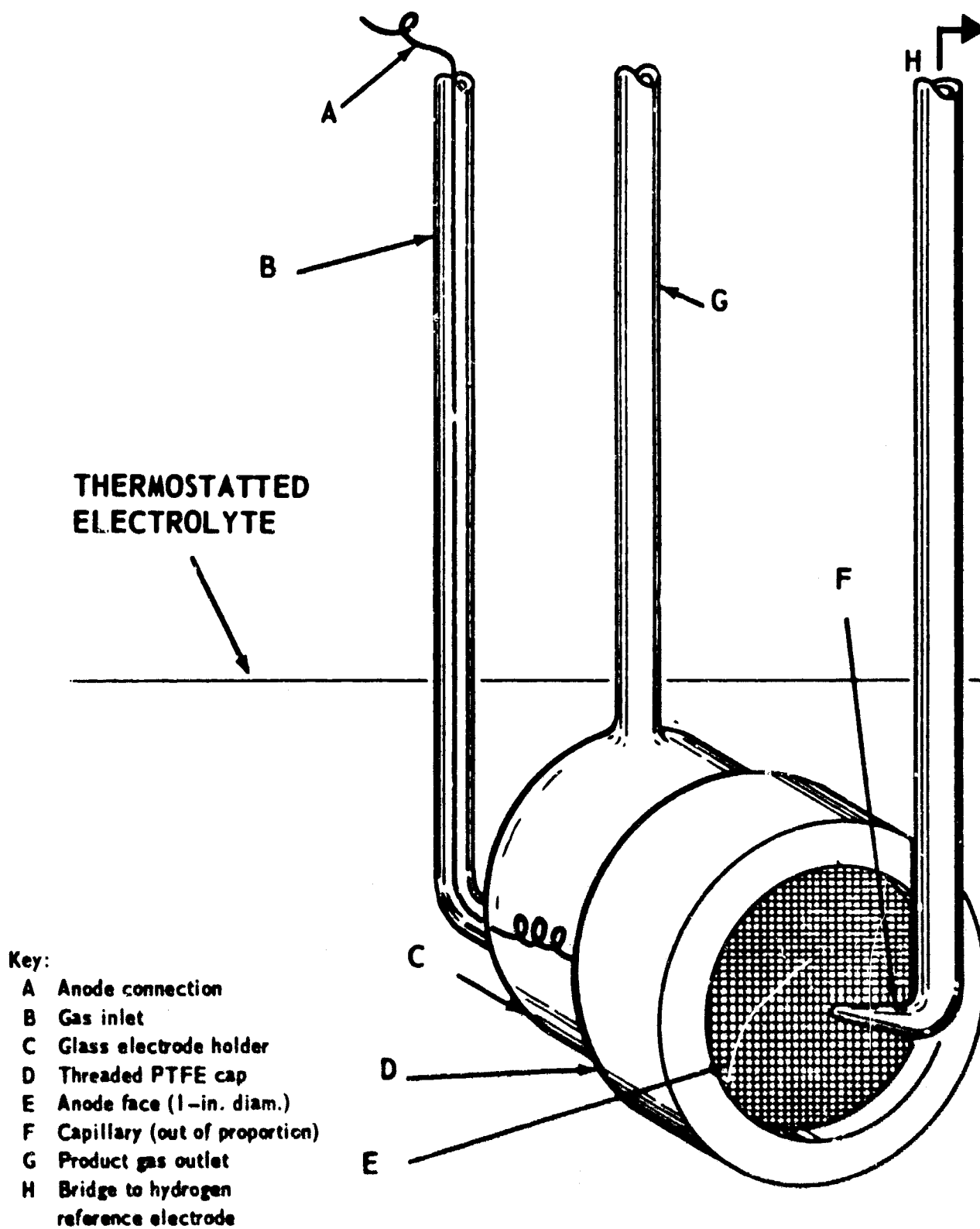
FIGURE 3.2-2

For polarization studies, a constant potential between the working and the reference electrodes was applied by the potentiostat for 2-3 minutes, and the current obtained at the predetermined potentials was recorded.

For all practical purposes, the concentration of phosphoric acid in the electrolysis cell at 100°C was 95-97%. It has been observed that 85% phosphoric increases in concentration to 95-97% when heated at 100°C for several hours. All potentials mentioned in this study are with respect to the hydrogen electrode. However, when the work was performed at 100°C, a corrective value* (due to temperature and concentration gradients) of 30 mV was subtracted from the potentials reported.

3.2.2 Sulfur Deposition Method

The different methods used by Binder et al[3-6] to cover the platinum black electrode with sulfur chemisorbate were: exposure of the electrode to hydrogen sulfide, cathodic reduction of sulfuric acid or sulfurous acid at high current densities, exposure to sulfur vapor or sulfur solution (in CS_2), and by use of sodium sulfide.

In this work sulfur was deposited chemically by using sodium sulfide ($Na_2S \cdot 9H_2O$) which, when added to acidic solutions, liberates hydrogen sulfide and deposits the sulfur at the platinum surface. This method was very easy to perform and had good reproducibility. A mono-layer of sulfur was assumed to be chemisorbed at the Pt black surface when the hydrogen adsorption peaks normally observed at the

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*The corrective value of 30 mV was observed when the reference hydrogen electrode was at room temperature and the electrolysis cell (having hydrogen atmosphere over the working electrode) was at 100°C.

platinum electrode disappeared during cyclic voltammetric measurements. This is discussed in more detail in Section 3.2.5.

It was observed experimentally that the addition of 0.4 ml of 0.58 $\underline{M}$ sodium sulfide to 250 ml of 6 $\underline{N}$ H_2SO_4 at room temperature in a closed vessel was sufficient to deposit a monolayer of sulfur on 5 cm^2 of AA-1 electrode (9 mg Pt black/cm^2). About one-half hour was sufficient to deposit the sulfur. The amount used is seven to eleven times higher than that theoretically required to cover the surface platinum atoms with a monolayer of sulfur, as calculated from the surface area of platinum black (30 m^2/g) and the packing density of platinum atoms in a smooth platinum surface,[7] assuming that one sulfur atom per platinum atom is required. Obviously, not all of the sulfur present as sulfide adds on to the platinum surface. In one experiment, 0.2 ml of the above sulfide solution covered 50% of the AA-1 electrode with sulfur. Thus, fractional coverage of the electrode with sulfur was obtained by v 'ng the proportionate amount of sodium sulfide. The exact mechanism of deposition is still not clear. It should, however, be mentioned that hydrogen gas was kept flowing at the back of the porous electrode while depositing sulfur. The function of hydrogen is assumed to be the removal of the platinum surface oxides so that sulfur chemisorption can take place on the electrode surface. This might also be accomplished by reducing the surface oxides electrochemically and then adding the sulfide.

3.2.3 Sulfur Removal Methods

Sulfur deposited on the platinum black electrodes could be removed by any of the following methods:

1. By oxidizing the electrode electrochemically to potentials > 0.80 V as discussed in Section 3.25. Sulfur is completely gone at 1.50 V.

2. By heating with dilute HNO_3.

3. By using the AC conductivity bridge (Model 16B2, Industrial Instruments, Inc., Cedar Grove, New Jersey) normally employed for resistance measurement. The AC wave has a peak-to-peak potential of 1.50 V, which is sufficient to oxidize sulfur deposited on the electrode.

3.2.4 Polarization Data

Current-potential behavior obtained with AA-2 and AA-3 electrodes is shown in Figures 3.2-3 to 5 and Table 3.2-1. The presence or absence of sulfur made no difference in performance on oxidation of pure hydrogen. However, a definite improvement in performance was observed for a sulfur-covered electrode when the hydrogen contained 1-10% carbon monoxide. Table 3.2-1 shows that for an AA-2 electrode, coverage with sulfur reduced the polarization on 10% CO from 480 mV at 100 mA/cm^2 to 170 mV (relative to pure hydrogen performance). Similarly, for an AA-3 electrode at 30 mA/cm^2, polarization relative to hydrogen was reduced from 400 mV to 210 mV. While these improvements are substantial, the performance of the sulfur-covered electrodes on impure hydrogen does not appear to be as good as can be obtained by other means. For example, an RA-2 electrode (5 mg noble metal/cm^2), tested in the same manner, showed a polarization relative to hydrogen of approximately 40 mV at 100 mA/cm^2.

Figure 3.2-5 shows the polarization curves obtained with an AA-2 electrode on which sulfur had been deposited and removed several times and many cyclic voltammograms and polarization curves had been obtained. This electrode was thus in use for several weeks. A decrease in performance on 10% CO compared to the new electrode was observed.

CURRENT–POTENTIAL CURVES IN 95–97% H_3PO_4 @ 100°C, AA–2 ANODE
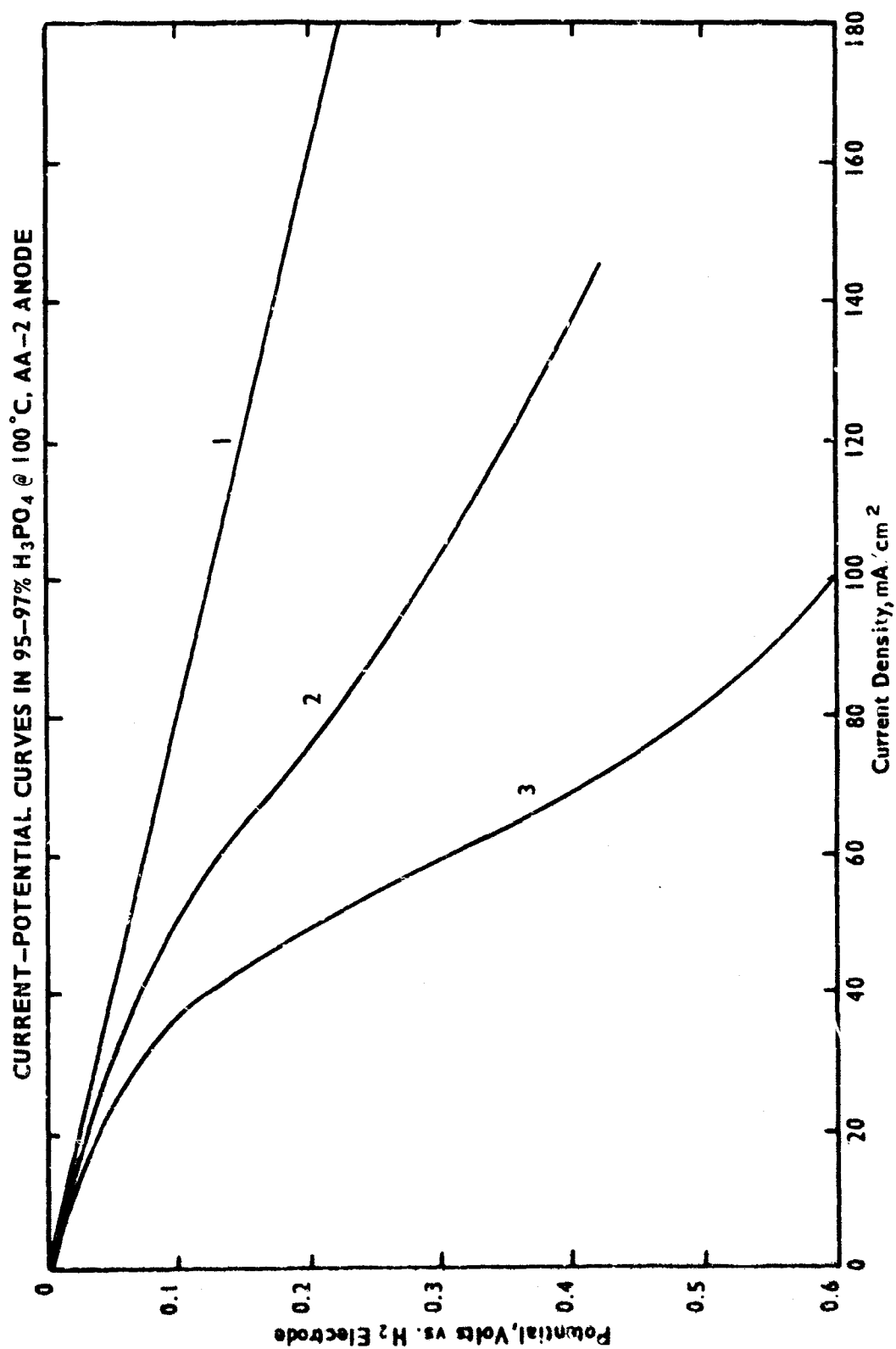
1. Pure H_2, with or without sulfur on anode
2. H_2 with 10% CO, sulfur–covered anode
3. H_2 with 10% CO, without sulfur on anode

FIGURE 3.2–3

- 24 -

CURRENT–POTENTIAL CURVES IN 95–97% H$_3$PO$_4$ @ 100°C, AA–3 ANODE

Current Density, mA/cm^2

Potential, Volts vs. H$_2$ Electrode
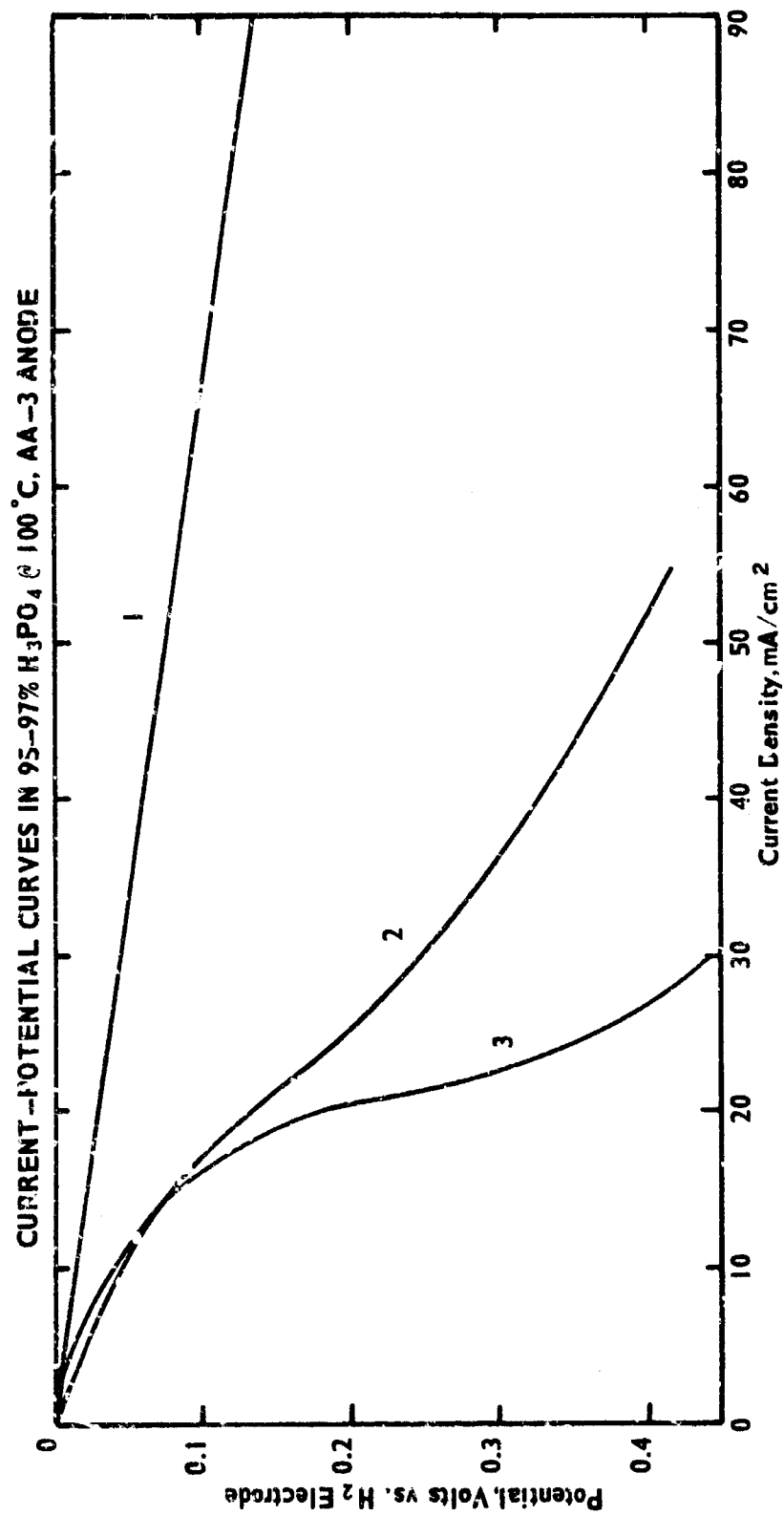
1. Pure H$_2$, with or without sulfur on anode
2. Hydrogen with 10% CO, sulfur–covered anode
3. Hydrogen with 10% CO, without sulfur on anode

FIGURE 3.2–4

CURRENT-POTENTIAL CURVES IN 95–97% H_3PO_4 @ 100°C, AA–2 ANODE (USED)
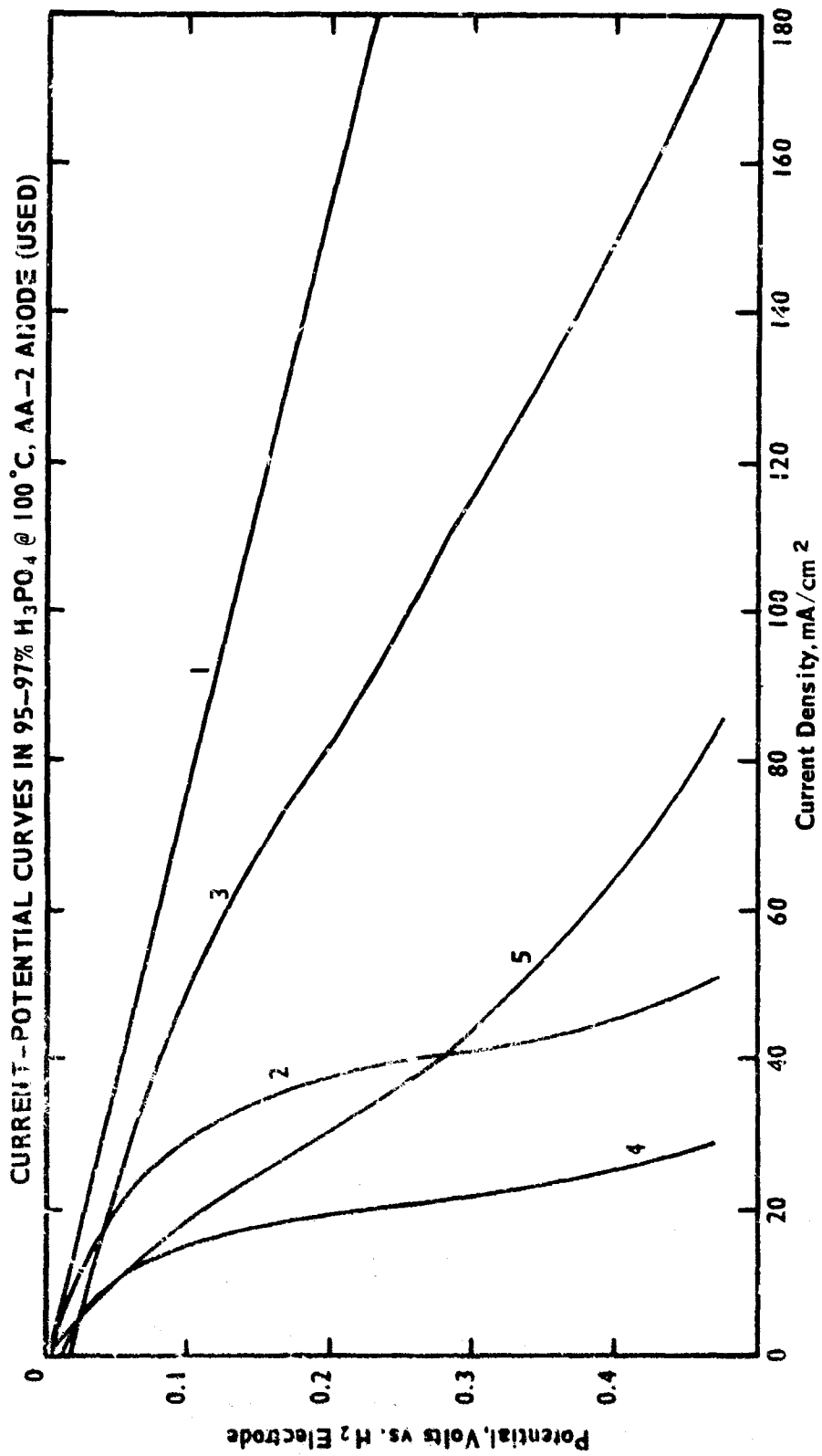
1. Pure H_2, with or without sulfur on anode
2. H_2 with 1% CO, without sulfur on anode
3. H_2 with 1% CO, sulfur–covered anode
4. H_2 with 10% CO, without sulfur on anode
5. H_2 with 10% CO, sulfur–covered anode

FIGURE 3.2–5

Table 3.2-1

Polarization Data at 100°C, 95-97% H_3PO_4

Anode Used	Potential at which 30 mA/cm² was Obtained		Potential at which 100 mA/cm² was Obtained	
	Pure H_2	90% H_2 10% CO	Pure H_2	90% H_2 10% CO
AA-3	0.04	0.44	--	--
AA-3$_{mono. S}$	0.04	0.25	--	--
AA-2	0.03	0.07	0.12	0.60
AA-2$_{mono. S}$	0.03	0.05	0.12	0.29

[1] Volts with respect to hydrogen reference electrode.

This electrode still showed no loss in performance when pure hydrogen
was used. Covering the electrode with a monolayer of sulfur improved
considerably the performance on hydrogen containing 1-10% CO, but to
a lesser extent than with the fresh electrode (Figure 3.2-3).

3.2.5 Cyclic Voltammetry

An electrochemical technique, cyclic voltammetry, was
utilized to ascertain the coverage of the platinum black surface with
sulfur. At room temperature, cyclic voltammograms (Figure 3.2-6) were
obtained for an AA-1 anode with and without sulfur in 85% H_3PO_4 and
6 N H_2SO_4. The hydrogen adsorption peaks for no sulfur coverage as
seen in curves 1 and 2 decreased proportionately as the electrode was
progressively covered with sulfur. Curve 3 shows 70% of the platinum
surface covered with sulfur while curve 4 has an apparent monolayer of
sulfur. At room temperature a platinum black surface covered completely
with sulfur fails to show hydrogen adsorption peaks (at 0.1 to 0.3 V),
shows a decrease in the double layer capacity region (0.3 to 0.5 V), and
shows no evolution of hydrogen even at 0.0 V. At 100°C, as seen in
Figure 3.2-7 (curves 1 and 2), the amount of hydrogen evolved at 0.07 V
with or without a monolayer of sulfur was about the same.

To obtain well-defined hydrogen adsorption peaks, the
distance of the reference probe from the test electrode is very critical.
The probe should be placed in the center of the electrode and be almost
touching it. The shift in potential between the hydrogen adsorption
peaks at room temperature using the two different electrolytes, Figure
3.2-6 (curves 1 and 2), may be due to the greater resistance in 85%
H_3PO_4 as shown below:

CYCLIC VOLTAMMOGRAMS, AA–I ANODES AT ROOM TEMPERATURE
4 mv/sec, N_2 atmosphere
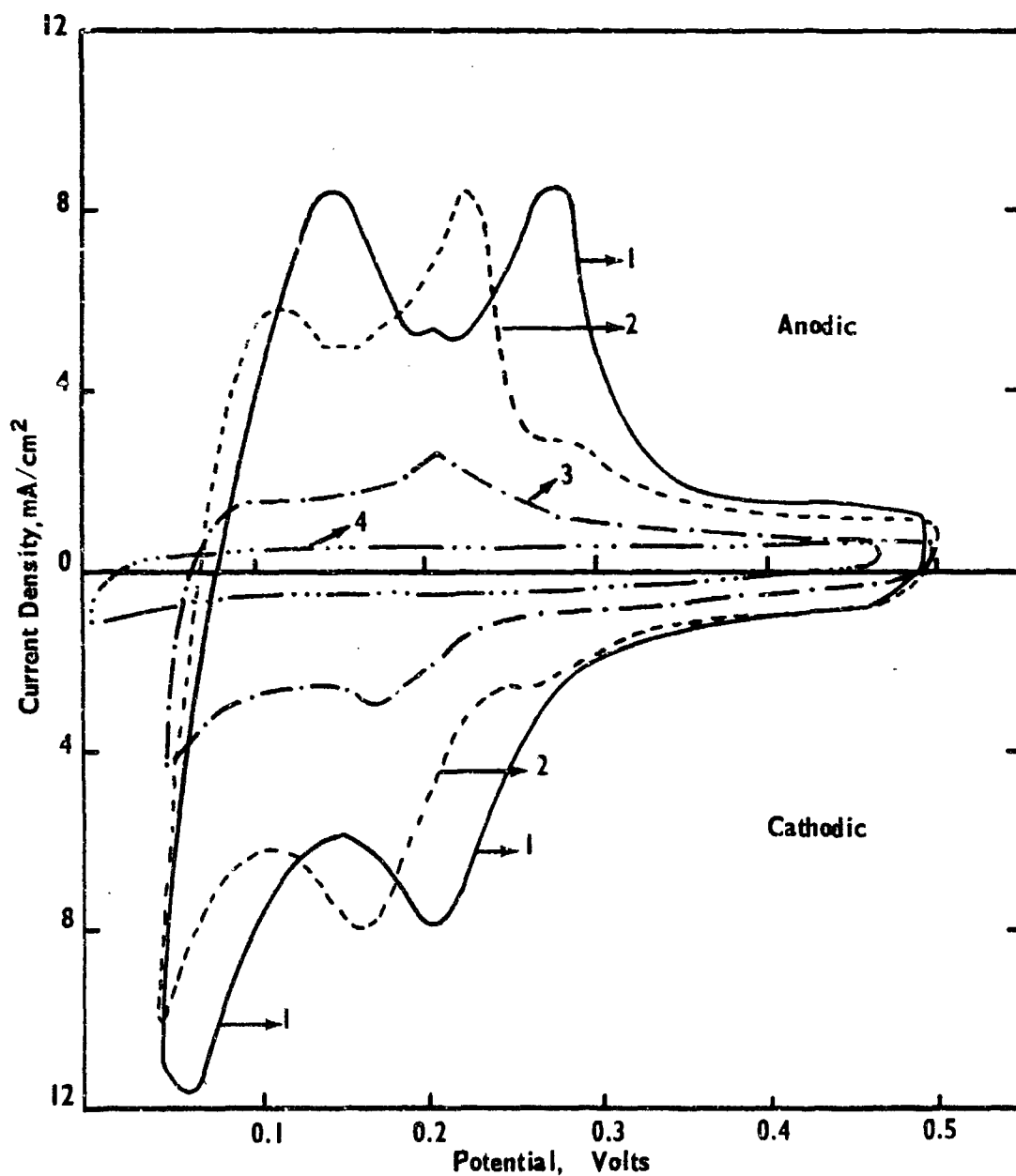
FIGURE 3.2–6
1. $6N H_2SO_4$, without sulfur
2. $85\% H_3PO_4$, without sulfur
3. $85\% H_3PO_4$, about 70% sulfur coverage
4. $85\% H_3PO_4$ Monolayer of sulfur

CYCLIC VOLTAMMOGRAMS, AA-2 ANODES AT 100°C
2.5 mv/sec, 95-97% H_3PO_4
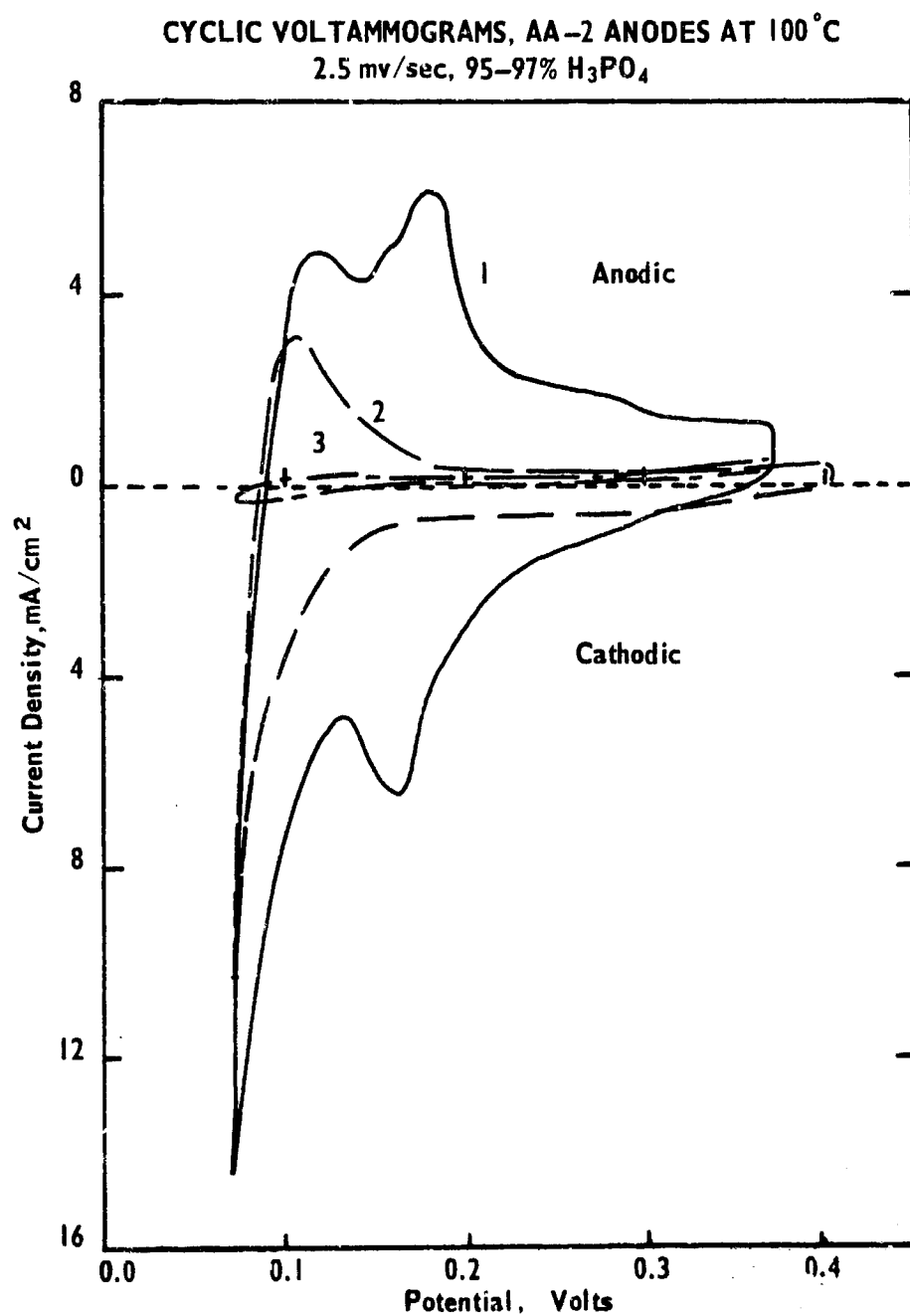
FIGURE 3.2-7   1. No sulfur, N_2 atmosphere
                 2. Monolayer of sulfur, N_2 atmosphere
                 3. CO atmosphere with or without sulfur

Resistance Between:

	Anode and Cathode	Anode and Reference
6 N H$_2$SO$_4$	1 Ω	600 Ω
85% H$_3$PO$_4$	5 Ω	6000 Ω

A cyclic voltammogram in the potential range of 0.7 to 1.4 V can also be utilized to determine the amount of sulfur present at the electrode surface. Comparison of curves 2 and 1, Figure 3.2-8, with and without a monolayer of sulfur respectively, shows that the increase in the area under the curve from 0.7 to 1.4 V was due to the oxidation of sulfur. Binder et al[3] have shown that for a monolayer of sulfur the above increase in area at room temperature in sulfuric acid is about four times that required for the hydrogen adsorption peaks (one electron change). suggesting that the sulfur is oxidized to sulfur dioxide. This is a "destructive" method of sulfur determination, since on a second cycle no excess area in the oxidation range of 0.7 to 1.4 V is observed.

3.2.5.1 Effect of Carbon Monoxide

The electrochemical oxidation of carbon monoxide near its thermodynamic potential ($E^\circ_{CO \to CO_2} = -0.116V$) is a highly desirable reaction. However, a very high activation polarization is usually observed. Carbon monoxide was adsorbed on the electrode surface by passing carbon monoxide at the back of the platinum black electrode for five minutes and then purging with nitrogen for five minutes. Cyclic voltammograms showed that the adsorbed carbon monoxide was oxidized at 0.91 V at room temperature and 0.60 V at 100°C in phosphoric acid (curves 4 and 3, Figure 3.2-8, respectively). With a sulfur-covered

CYCLIC VOLTAMMOGRAMS, AA-2 ANODES AT 100°C
3 mv/sec, 95-97% H_3PO_4, N_2 atmosphere

Anodic

Cathodic

Potential, Volts

Current Density, mA/cm²
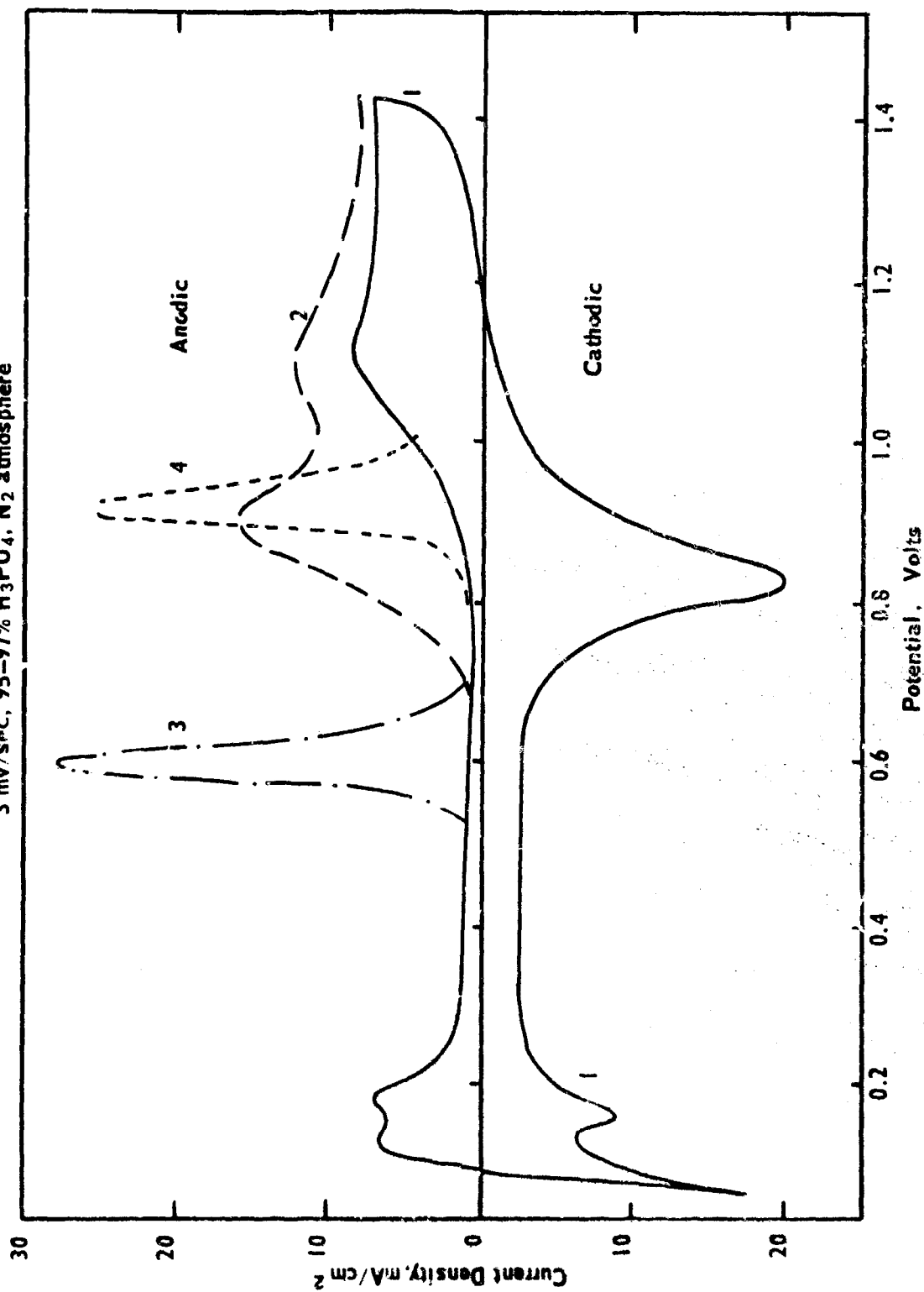
1. Without sulfur
2. With monolayer of sulfur
3. Oxidation of adsorbed CO at 100°C (without sulfur)
4. Oxidation of adsorbed CO at room temperature (without sulfur)

FIGURE 3.2-8

platinum black electrode similarly treated in phosphoric acid at 100°C, no adsorbed carbon monoxide peak was observed. Thus, carbon monoxide is probably not strongly adsorbed at the Pt-S surface. This may be one of the reasons for the improvement in the performance of the Pt-S anode as compared to the platinum surface. Binder[5] et al also obtained similar results in sulfuric acid.

Using a carbon monoxide atmosphere instead of a nitrogen atmosphere at the back of the working electrode, curve 3, Figure 3.2-7, was obtained. The results were similar whether or not the electrodes were sulfur coated. The double layer capacity was decreased considerably, and hydrogen adsorption as well as hydrogen evolution peaks were eliminated.

3.2.5.2 Stability in Phosphoric Acid of Sulfur Deposited on Platinum Black

A sulfur-coated electrode having an open circuit potential of about 0.3 V was kept overnight (18 hours) at 100°C in 95-97% H_3PO_4 under nitrogen atmosphere. Next day the open circuit potential was 0.9 V. A cyclic voltammogram showed well-defined hydrogen adsorption peaks indicating the complete removal of sulfur under the above conditions. It has been shown previously (Figure 3.2-8) that sulfur is oxidized in the potential range of 0.7 to 1.4 V. Thus, keeping the sulfur-coated electrode on open circuit at 100°C caused the removal of sulfur. Another sulfur-coated electrode was controlled potentiostatically at 0.30 V, overnight (18 hours) at 100°C in 95-97% H_3PO_4. Next day a cyclic voltammogram showed no hydrogen adsorption peaks and so no loss in sulfur occurred. It may thus be inferred that as long as the potential of the sulfur-coated electrode is less than the oxidation potential of sulfur, i.e., less than 0.7 V, sulfur will remain on the electrode surface.

In another experiment, a sulfur-coated platinum black electrode was kept on open circuit at 100°C in 95-97% H_3PO_4 for about five hours under a nitrogen atmosphere. The cyclic voltammogram (curve 2, Figure 3.2-9) showed a new cathodic peak at 0.36 V. The identity of the compound thus reduced is not yet established, but it may be the oxidized product of sulfur. Further work is needed to elucidate this new reduction peak.

3.3 Matrix Development

3.3.1 Objectives

The program objectives require a matrix which can operate stably at 150-200°C for more than 1,000 hours. Work was started to develop a 15-30 mil thick matrix having the following combination of properties at 150-200°C: (1) weight and dimensional stability in all concentrations of H_3PO_4, (2) sustained wettability, (3) resistivity $\leq$ 0.8 ohm-cm^2, (4) bubble pressure $\geq$ 5 psi, (5) sufficient mechanical strength, and (6) no significant electronic conduction. Matrices being investigated for this program are of the filled-PTFE type, in which a small amount of PTFE (as little as 2-10% by volume) is used as a binder for a wettable, corrosion-resistant filler material. In the TA-1 matrix, which has been used extensively in life tests run under this contract, the filler material is etched PTFE fiber. TA-1 matrix is satisfactory with respect to criteria (3) through (6) above, but has apparent drawbacks with respect to dimensional stability, and possibly also with respect to sustained wettability. The overall objective of the matrix development program is to evaluate alternative filler materials and process modifications directed toward overcoming these drawbacks.

CYCLIC VOLTAMMOGRAMS, AA-2 ANODE AT 100°C
(After five hours on open circuit)
3.2 mv/sec, 95-97% H₃PO₄, N₂ atmosphere
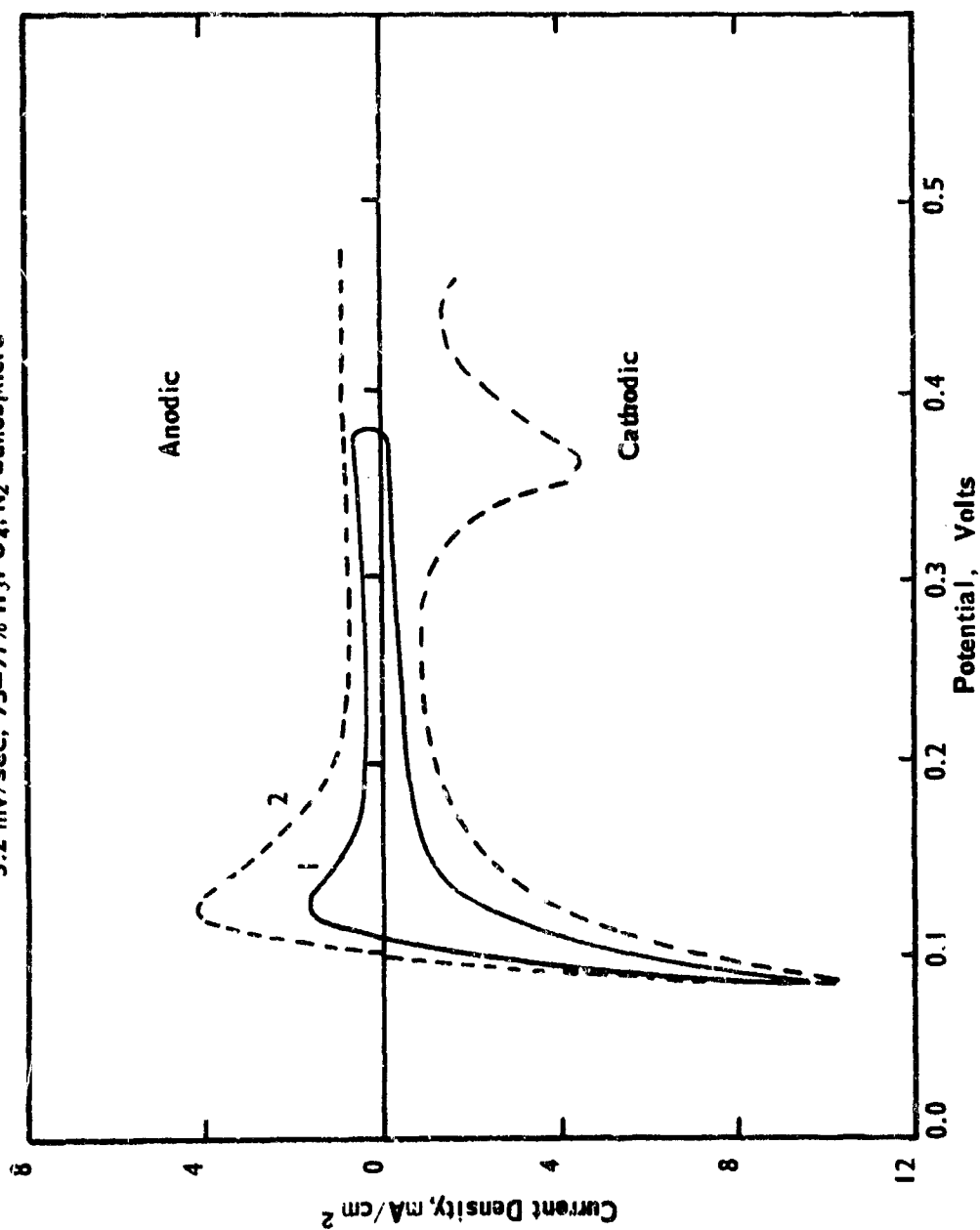
FIGURE 3.2-9

1. With monolayer of sulfur
2. After five hours on open circuit

3.3.2 Corrosion Resistance of Matrix Fillers at 150-200°C

PTFE is reported to be completely inert to all chemicals except molten alkali metals and fluorine.[8] Corrosion tests of PTFE fiber in 100% H_3PO_4 at 200°C showed no significant weight loss after 10 days.[1-b] In the current program, powders or fibers of quartz, tantalum pentoxide, and zirconium pyrophosphate were also investigated as promising filler materials in corrosion tests with 100% H_3PO_4 at 150-200°C for approximately 300 hours.

At each temperature, duplicate 2 g samples were immersed in 220 g of the acid within sealed PTFE beakers. This is a more severe test than the material would face in an operating matrix type fuel cell, in which the filler material would be exposed to less than about five times its weight of electrolyte. Possible re-precipitation of any soluble corrosion product through cooling was minimized by centrifuging the corrosion-tested sample, when necessary, and then decanting most of the acid at temperatures generally only 20-40°C below the test temperature. (No precipitation of solids occurred when the filtrates were cooled to room temperature, however.) The solids were then filtered, washed free of acid, dried, weighed, and examined microscopically. Table 3.3-1 shows the corrosion resistance of these materials.

3.3.2.1 Fused Quartz

A commercial fused quartz fiber (fine quartz wool - Thermal American Fused Quartz Company) was evaluated. This fiber, > 99% SiO_2, is very brittle and mashes easily to a powder. Weight loss in phosphoric acid at 150-200°C was negligible. The structure of the unmashed fiber degraded somewhat at 150°C, evidenced either by local

Table 3.3-1

MATRIX FILLERS: CORROSION IN 100% H_3PO_4 AT 150-200°C

Duration: 280-350 hours

Material	Form	Source	Weight Loss(a), %, at		Structural Degradation at:	
			150°C	200°C	150°C	200°C
Fused Quartz	Fiber	Thermal American	1	1	Slight	Complete
		Fused Quartz Company				
Ta_2O_5	Powder	Fisher Scientific	1	11	No	None
Ta_2O_5	Fiber	Union Carbide	13	76	Slight	Considerable
Ta_2O_5	Cloth No. 11	Union Carbide	28	(b)	-	-
ZrP_2O_7	Powder	Tizom Chemical Corporation	22	22	-	-

(a) Average of duplicate samples

(b) Difficulties in determining dry weight; corrosion appeared to be considerable.

etching of the fiber wall or by nearly uniform reduction of the fiber diameter (Figures 3.3-1, A and B). Complete degradation occurred at 200°C (Figure 3.3-1 C). The structure of mashed fiber degraded considerably at 150°C and completely at 200°C (Figures 3.3-2, A-C). The refractive index of the reaction product is below 1.440 and probably below 1.430, compared to 1.458 - 1.460 for the fiber. Infrared and X-ray diffraction data indicate that this low index material is a silica hydrogel.

3.3.2.2 Tantalum Pentoxide

Tantalum pentoxide powder (Fisher Scientific Company) had negligible weight loss at 150°C and 11% loss at 200°C. Microscopic examination indicated no structural degradation of the undissolved material at either temperature (Figure 3.3-3, A-C).

A tantalum pentoxide fiber (Union Carbide) had 13% weight loss at 150°C, with only slight degradation of the undissolved fiber, and considerable weight loss (76%) and structural degradation at 200°C (Figure 3.3-4, A-C).

Tantalum pentoxide cloth No. 11 (Union Carbide) had greater weight loss at 150°C (28%). Experimental difficulties prevented weight loss measurements at 200°C, but visual observation indicated these losses to be considerable.

3.3.2.3 Zirconium Pyrophosphate

Zirconium pyrophosphate (Tizon Chemical Company) had substantial weight loss (22%) at both 150°C and 200°C. Losses of this magnitude in beaker corrosion tests do not necessarily rule out a material which may be more stable within an operating cell where there is no

FUSED QUARTZ FIBER
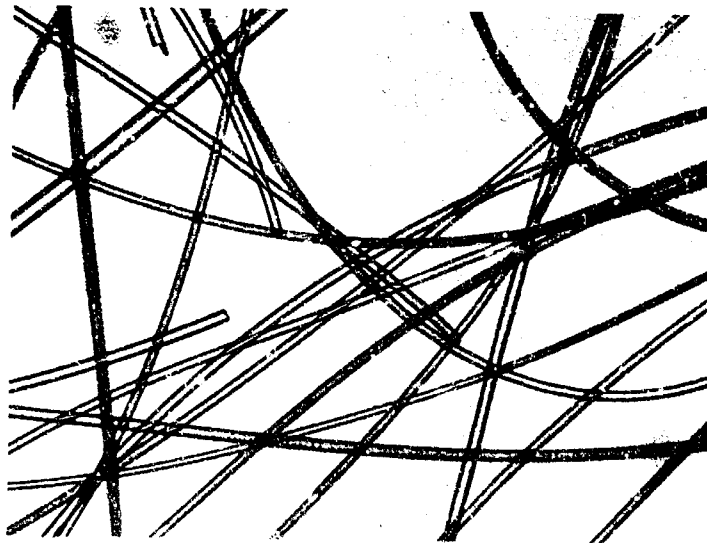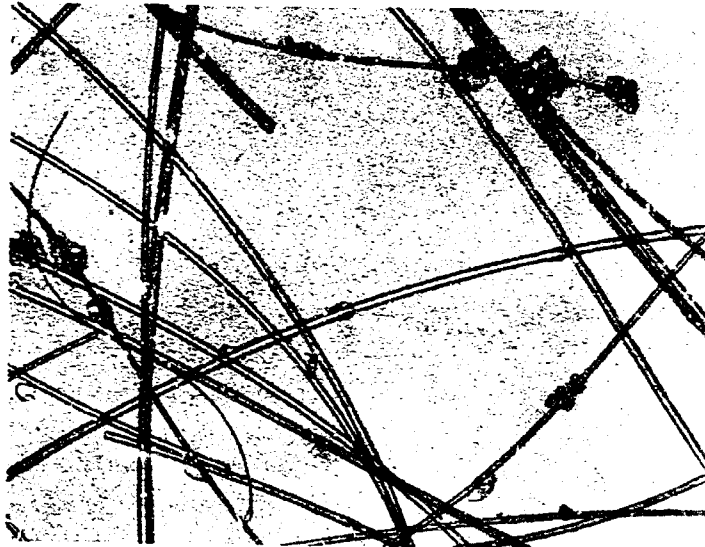
Before and after corrosion tests (Magnification: 100X)

(a) Unexposed

(b) Exposed 300 hours in 100% H_3PO_4 at 150°C
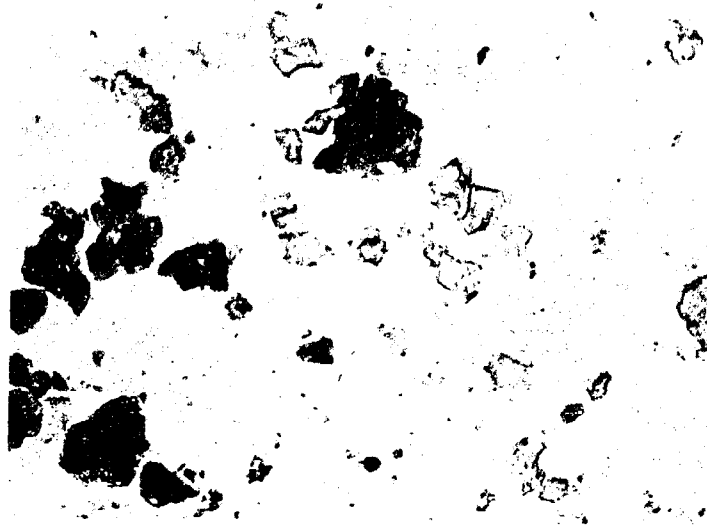
(c) Exposed 300 hours in 100% H_3PO_4 at 200°C

FIGURE 3.3-1

(MASHED) FUSED QUARTZ FIBER
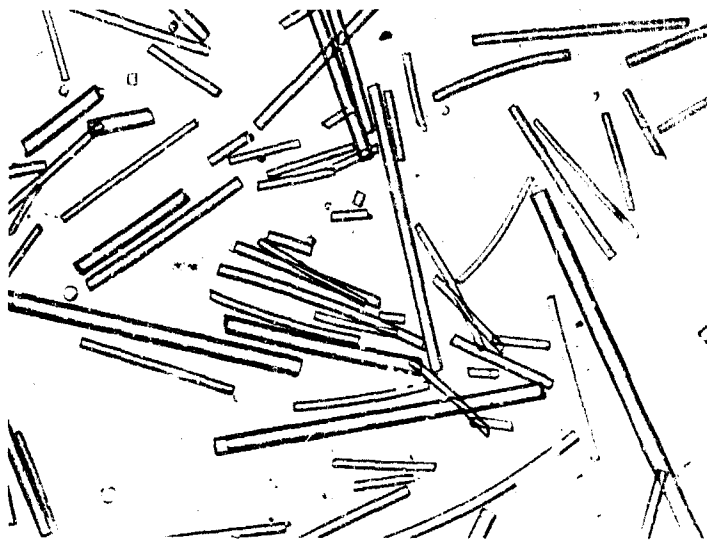
Before and after corrosion tests (Magnification: 100X)
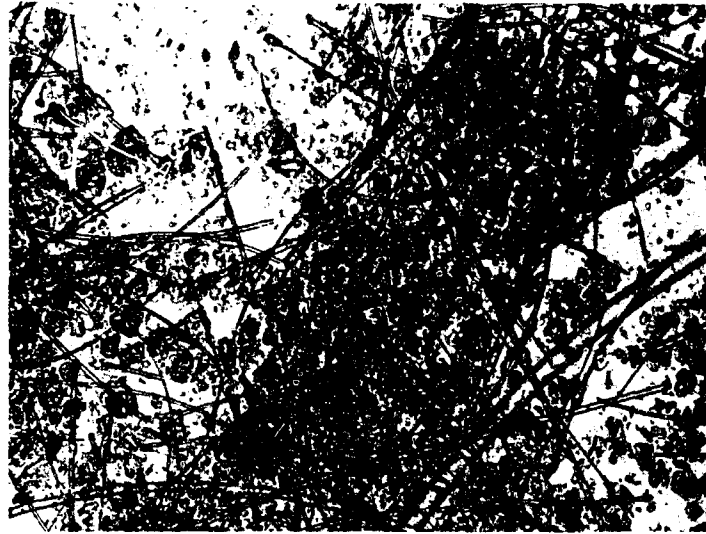
(a) Unexposed

(b) Exposed 300 hours in 100% H_3PO_4 at 150 °C

(c) Exposed 300 hours in 100% H_3PO_4 at 200 °C

FIGURE 3.3-2

TANTALUM PENTOXIDE POWDER

Before and after corrosion tests (Magnification: 500X)
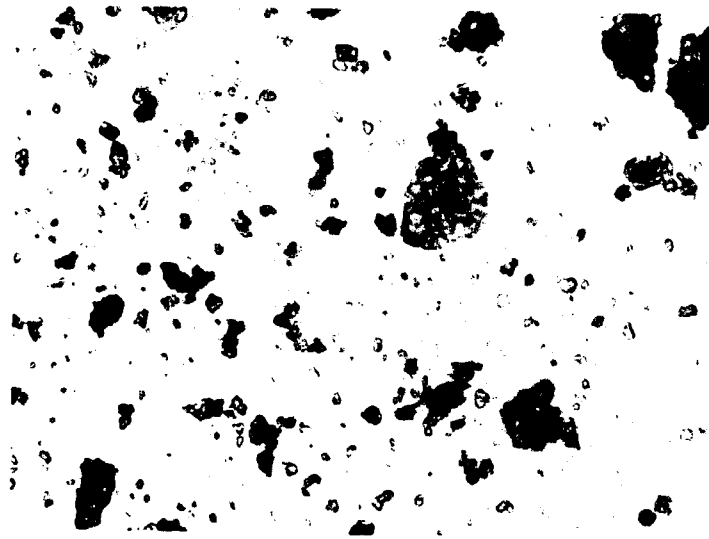
(a) Unexposed

(b) Exposed 300 hours in 100% H_3PO_4 at 150 °C
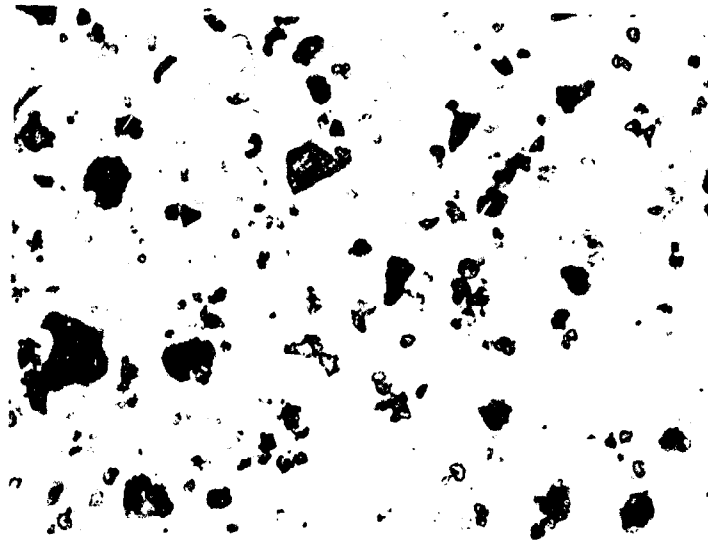
(c) Exposed 300 hours in 100% H_3PO_4 at 200 °C

FIGURE 3.3-3

TANTALUM PENTOXIDE FIBER

Before and after corrosion tests (Magnification: 500X)
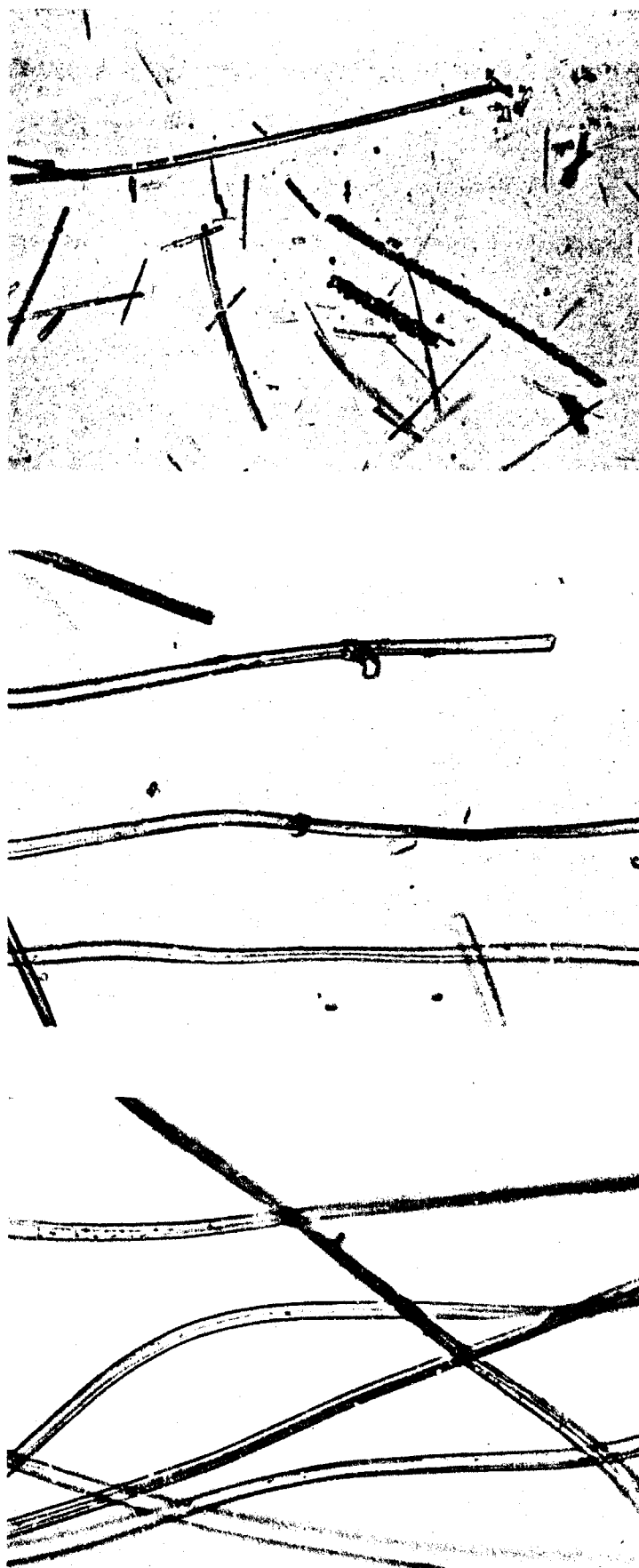
(a) Unexposed

(b) Exposed 300 hours in 100% H_3PO_4 at 150°C

(c) Exposed 300 hours in 100% H_3PO_4 at 200°C

FIGURE 3.3—4

excess electrolyte. This is indicated directly by the reasonably stable
2,000-hour performance in one test with the TA-2 matrix at 150°C
(HCLT-78).[2-a] The decline rate in this test averaged 4 mV/100 hours
during 1,000 hours at 60 mA/cm^2, and 7 mV/100 hours during an additional
1,000 hours at 100 mA/cm^2. Furthermore, extensive stable performance
data in alkaline matrix fuel cells have been reported[9] for periods up
to 9,700 hours under conditions which caused 40% weight loss of the
matrix (asbestos) in beaker corrosion tests.[10] Nevertheless, the three-
quarters of the zirconium pyrophosphate remaining uncorroded may be a
more promising filler, particularly since the equal weight loss data at
150°C and 200°C suggest that this remaining material may be completely
stable.

3.3.3 Matrices

Filled-PTFE matrices, containing 95% by weight of PTFE
fiber (TA-1), zirconium pyrophosphate (TA-2), or quartz powders or fibers
were studied. The TA-1 matrix designated "original" and the TA-2 matrix
were used previously in the program. A "modified TA-1" matrix has the
same composition as the original but is somewhat thicker.

The commercial quartz powders and fibers (Thermal American
Fused Quartz Company) used in these matrices are made of the same grade
of fused quartz as the fiber which showed negligible weight loss in
phosphoric acid at 150-200°C. Figure 3.3-5, A-C, shows their configura-
tions. The fine powder (Spectrosil®) has particles mostly 1-70 μ in
minimum dimension with some particles as large as 120 μ. The coarser
powder (Vitreosil®) particles are mostly 40-220 μ. The fiber, designated
coarse wool, has diameters of 3 to about 25 μ with the overwhelming
majority in the range 5-14 μ.

FORMS OF FUSED QUARTZ USED IN MATRICES

(Magnification: 200X)
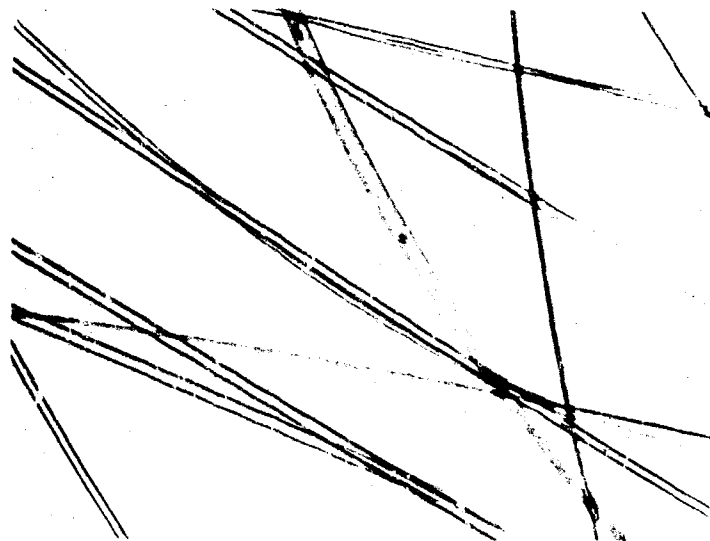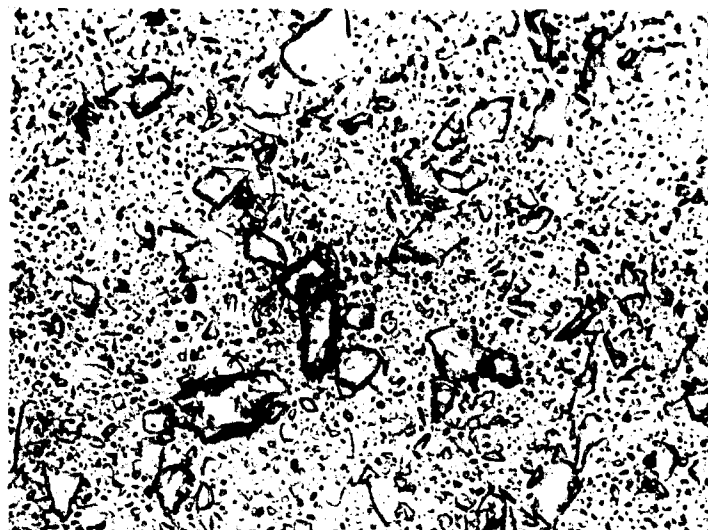
(c) Powder
(Vitreosil) ®

(b) Fine Powder
(Spectrosil) ®

(a) Fiber

FIGURE 3.3-5

3.3.4 Matrix Property Measurements

Matrix porosity was determined from the total volume and dry weight of two-inch disc samples, and the specific gravity of the solids. The average of five thickness measurements was used in determining the total volume. The percent of the pore volume filled with liquid was calculated from these measurements together with the wet weight of the sample and the specific gravity of the liquid.

Bubble pressures in water at room temperature were measured in a Gelman filter on one-inch diameter discs. The samples usually had 90-100% of their pore volume filled with liquid. A tube from the space on one side of the matrix was immersed in a beaker of water just below the surface. Air pressure on the other side was raised continuously at the rate of 3-6 psi/minute. Preliminary tests indicated that the pressure rise rate is not critical since no significant change in the observed bubble pressure resulted when the pressure was raised incrementally at 1 psi/minute. The pressure which first produced a steady stream of bubbles in the beaker of water was taken as the bubble pressure. Reported bubble pressures are mostly the average of three measurements.

Shrinkage was measured in 100% H_3PO_4 at 150-200°C on discs which were normally two inches in diameter, although occasionally somewhat smaller pieces were used. The samples were immersed under a one-inch depth of 70-150 ml of the 100% acid in PTFE beakers. Area dimensions and five thickness points were measured three or four times during 20 hours.

Resistivity was measured by a Keithley milliohmeter during life tests at 150°C and 95-100% H_3PO_4 in 2-inch x 2-inch cells (26 cm^2 active area). Values reported are for the minimum resistivity which is generally reached within the first 100 hours of the test and which averaged 0.10-0.15 ohm-cm^2 below the initial resistivity.

3.3.5 Properties of Untreated Matrices

Table 3.3-2 shows properties of matrices received water-wet as usual. The TA-1 (original and modified), TA-2, and quartz fiber-PTFE matrices all have satisfactory combinations of resistivity in H_3PO_4 at 150°C (0.42-0.57 ohm-cm^2) and bubble pressure in water (6-13 psi). As expected, resistivity decreases with increasing porosity. Thus, although they are thicker, both TA-1 matrices have lower resistivities than the TA-2 and quartz fiber-PTFE matrices. The matrices containing quartz powders are less porous than that filled with quartz fiber and are probably more resistive. The modified TA-1 matrix 6 mils thicker than the original, has substantially better bubble pressure than the original, at no sacrifice in porosity or resistivity.

None of the untreated matrices evaluated for shrinkage are dimensionally stable in phosphoric acid at 150-200°C. Thus, they lost 16-57% of their area and thickened 44-92% during the 310-hour exposure. For all of the matrices, nearly all of the area loss occurred within the first 72 hours (Figures 3.3-6 and 7). Thickening was either continuous during 310 hours (TA-1 at 150-200°C and TA-2 at 150°C), nearly arrested after 72 hours (TA-2 at 200°C), or partially reversed after 72 hours (quartz fiber-PTFE at 150-200°C).

Table 3.3-2

Properties of Untreated Filled-PTFE Matrices[a]

Matrix Filler	Water-Wet Thickness (Mils)	Water-Wet Porosity (%)	Bubble Pressure (psi)[b]	Resistivity (Ohm-cm²)[c]	Shrinkage in 100% H₃PO₄ at:[d] 150°C			200°C			Condition After Exposure at 150-200°C
					Change in Area (%)	Thickness (%)	Porosity (%)	Change in Area (%)	Thickness (%)	Porosity (%)	
PTFE Fiber (Original TA-1)	29	83	6	0.47	-16	54	-	-21	54	-	Flexible
PTFE Fiber (Modified TA-1)	35	34	13	0.42	(e)	(e)	(e)	(e)	(e)	(e)	-
Zirconium Pyrophosphate Powder (TA-2)	22	79	9	0.55	-57	48	-	-57	44	-	Flexible
Fine Quartz Powder	23	65	11	-	-	-	-	-23	94	-	Brittle & cracked
Quartz Powder	35	62	7	-	-	-	-	-19	60	-	Brittle
Quartz Powder[f]	22	69	6	-	-	-	-	-36	92	-	Brittle & cracked
Quartz Fiber	25	78	8	0.57	-34	61	-	-34	67	-	Brittle & cracked

(a) 95% filler by weight.

(b) Measured in water on one-inch diameter discs, at room temperature.

(c) Measured in 95-100% H₃PO₄ at 150°C. Value for original TA-1 averaged from 42 measurements in range of 0.26-0.75 ohm-cm². Value for TA-2 averaged from five measurements in range of 0.49-0.64 ohm-cm². Values for other matrices are from single measurements.

(d) Measured for 310 hours on two -1-inch diameter discs.

(e) Measurements in progress.

(f) Different thickness and porosity than other quartz powder-PTFE matrix.

DIMENSIONAL CHANGES WITH TIME IN 100% H₃PO₄ AT 150°C
(Untreated Matrices)
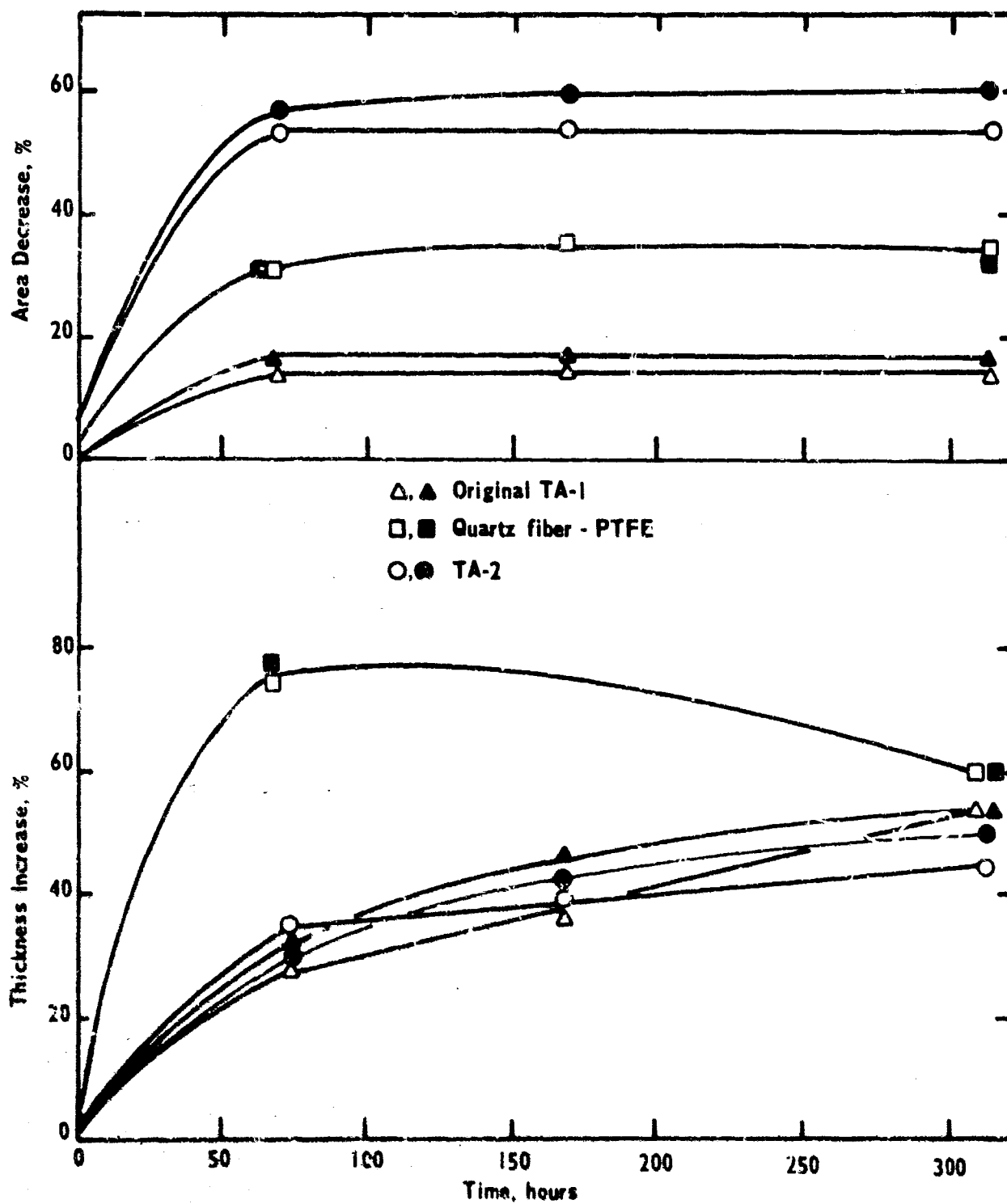
FIGURE 3.3-6

DIMENSIONAL CHANGES WITH TIME IN 100% H_3PO_4 AT 200°C
(Untreated Matrices)
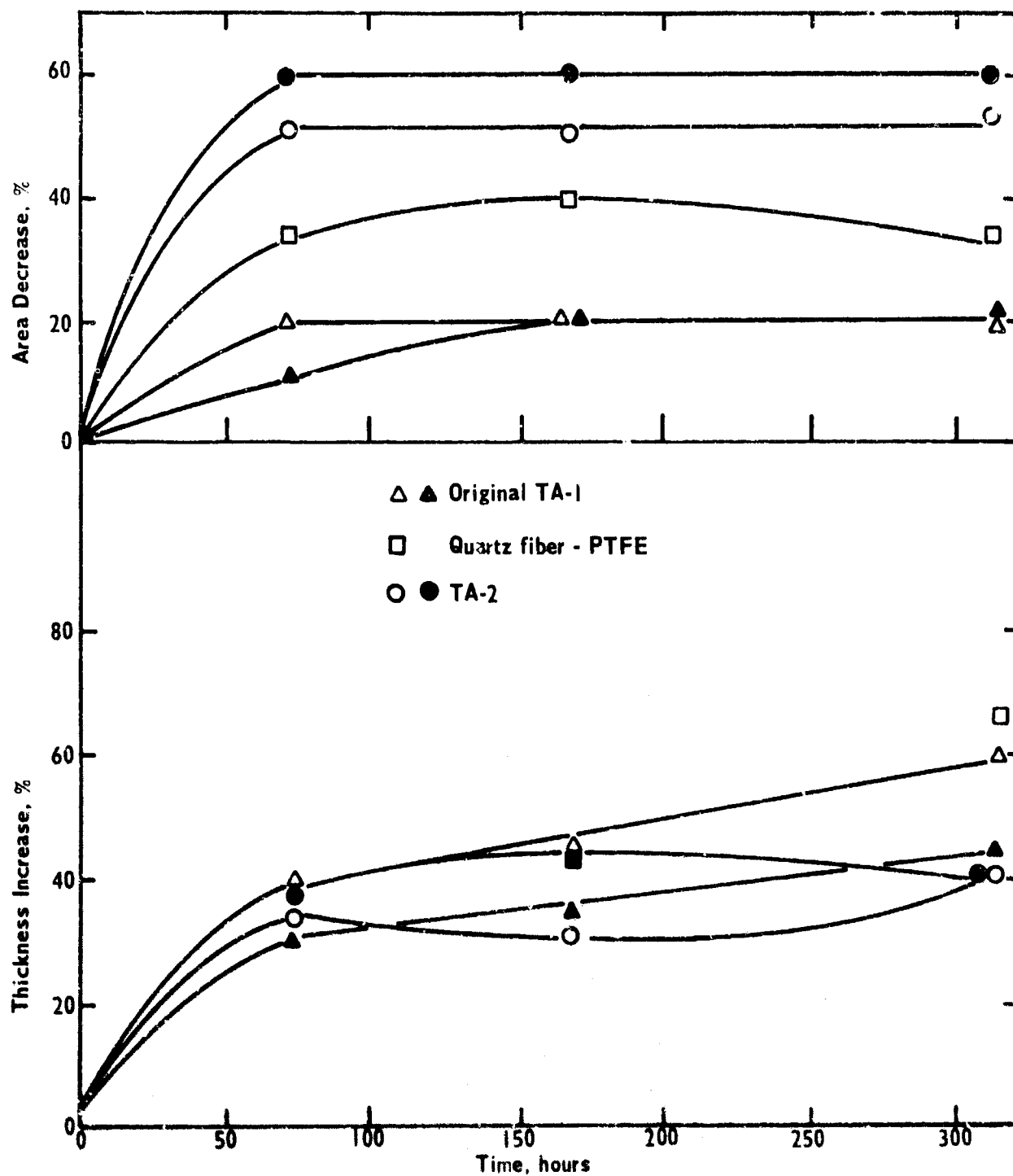
FIGURE 3.3 7

The TA-1 and TA-2 matrices remained flexible after exposure. However, all of the quartz-filled matrices became brittle and, in some instances, cracked. The possibility of minimizing embrittlement by using quartz pre-digested in hot H_3PO_4 or by reducing its percentage in the matrix will be investigated.

3.3.6 Properties of Post-Treated Matrices

When the matrix is constrained within an operating cell, the tendency to shrink sets up strains which may lead to eventual mechanical failure. In view of the dimensional instability observed with a variety of filler types, configurations, particle sizes and initial porosity, it appears that processing modifications may be required for filled-PTFE matrices. During this period the matrices were modified by post-treatments. These included pre-shrinkage through drying and pre-shrinkage followed either by heating somewhat below the sintering temperature of solid PTFE or by sintering at 340-360°C.

3.3.6.1 Dried Matrices

For all matrices except the modified TA-1, two inch water-wet discs were dried overnight to constant weight at 80-90°C. A 10 in. x 11 in. sheet of the modified TA-1 matrix was dried in the same manner. Dimensional changes caused by drying are shown in Table 3.3-3. The TA-1 matrices had moderate area losses (8-16%) and more substantial thickness losses (22-30%). Area and thickness losses were small or moderate for all of the quartz-filled matrices (3-17%) and more substantial for the TA-2 matrix. The resulting losses in porosity were 4-10% for TA-1 and quartz-filled matrices and 16% for TA-2.

Table 3.3-3

Properties of Dried and Re-Wet Matrices

Matrix Filler	Dried			Re-Wet[a]							Shrinkage in 400% R.H. at 180°C[d]									Condition After Exposure at 200°C
	Change in		Porosity (%)	Water			95% H₃PO₄		Bubble[b] Pressure (psi)	Resistivity[b] (Ohm-cm²)	Change in		Porosity (%)	Change in		Porosity (%)				
	Area (%)	Thickness (%)		First Re-wet in	Porosity (%)	Pore Volume Filled With Water (%)	Porosity (%)	Pore Volume Filled With Acid (%)			Area (%)	Thickness (%)		Area (%)	Thickness (%)					
PTFE Fiber (Original TA-1)	-4	-8	74	Water	75	92	74	23	2.5	–	4	5	75	-6	-8	76				Flexible
PTFE Fiber (Modified TA-1)	-15	-22	77	Water	75	96	76	123	2.1	–	–	–	–	–	–	–				–
				1% FC-128[e]	77	96	–	–	8	0.6	(4)	(6)	(8)	(6)	(6)	(6)				(?)
				Ethanol[f]	78	134	–	–	6	–	–	–	–	–	–	–				–
				Conc. Acetic Acid	79	97	–	–	8	–										
Zirconium Pyrophosphate Powder (TA-2)	-24	-23	63	Water	65	61	65	38	4	–	9	8	80	-7	-8	80				Flexible
Fine Quartz Powder	-15	-7	65	Water	55	96	56	107	6	–	–	–	–	-8	-8	76				Brittle, cracked
Quartz Powder	-4	-6	70	Water	57	41	56	94	2.4	–	–	–	–	-4	-5	67				Brittle
Quartz Powder[h]	-6	-3	67	Water	64	74	64	92	2.0	–	–	–	–	-9	-9	74				Brittle
Quartz Fiber	-2	-47	74	Water	77	71	72	96	–	–	1	9	82	-6	-6	80				Brittle & cracked

(a) Re-wet under vacuum for 1 hours unless noted otherwise.
(b) Measured in water on one-inch diameter discs, at room temperature.
(c) Measured in 400% R.H. at 180°C.
(d) Measured for 16 hours in one-inch diameter discs. Area and thickness changes based on the dimensions of the dried and re-wet sample.
(e) 1% solution of FC-128 (3M Company) in water.
(f) Re-wet by overnight immersion.
(g) Measurements in progress.
(h) Different thickness and porosity than other quartz powder-PTFE matrix.

All of the dried matrices were re-wet directly in water
and in 85% H_3PO_4 under 28-29 in. vacuum for 2-4 hours. In addition,
the modified TA-1 was first re-wet in low surface tension liquids
including ethanol, concentrated acetic acid, and a 1% water solution
of FC-128, a perfluorinated surfactant (3-M Company). Since the
surface tensions of all of these liquids (17-28 dynes/cm^2)[11,12] are
below that of the critical surface tension of wetting of etched PTFE
(30 dynes/cm^2)[13], they should in principle completely wet the matrix
surfaces. Re-wetting with acetic acid and 1% FC-128 was done under
vacuum for 2-4 hours, the former at 28-29 inches vacuum and the latter
at 24 inches in order to prevent foaming. Ethanol re-wetting involved
overnight immersion at atmospheric pressure. The low surface tension
liquids were then extracted by water during three 15-minute soaks
followed by overnight immersion.

Table 3.3-3 shows that with nearly all matrices more
than 90% of the pore volume was filled with water or acid. All of the
values above 90% are for samples which were re-wet under vacuum for a
total of four hours if they were less than 90% filled after the first
two hours. The lower values for the TA-2 and the original TA-1 were
obtained early in the program and are for vacuum immersion of 2 to 2-1/2
hours. It is possible that they would increase with longer immersion.
Porosity changes caused by re-wetting were only 0-3%.

Properties of the dried and re-wet matrices are also
shown in Table 3.3-5. Comparison with Table 3.3-2 shows that the bubble
pressures of the dried and re-wet matrices are mostly 4-6 psi lower than
those of the untreated ones. The lower bubble pressures might result
from incomplete filling of only a few matrix pores. Despite this

lowering, the modified TA-1 and fine quartz powder-PTFE matrices have acceptable bubble pressure in water (> 5 psi) after drying and re-wetting.

Comparison of Tables 3.3-2 and 3.3-3 for all of the matrices studied shows that drying and re-wetting nearly eliminates area loss in H_3PO_4 at 150-200°C during 310 hours. This treatment also nearly eliminated thickening of the original TA-1 matrix at 150-200°C and of the TA-2 matrix at 200°C. Thickening of the quartz-PTFE matrices at 200°C was reduced, though not by more than one-half. All area changes but not all thickness changes occurred within the first 72 hours (Figures 3.3-8 and 9).

3.3.6.2 Dried and Heated Matrices

Two-inch water-wet discs were dried at 80-90°C and then heated at 250-300°C and cooled rapidly. While these temperatures are below the sintering temperature of solid PTFE (327°C), heating of the original TA-1 matrix at about 300°C for only 5 minutes appeared to cause partial sintering, as indicated by X-ray diffraction measurements which showed a decrease in crystallinity. This probably occurred because of the fine subdivision of at least some of the PTFE.

Preliminary work showed that heating times of 5 minutes to 16 hours gave essentially the same dimensional changes during heating and during exposure in hot acid (Figure 3.3-10) with both the original TA-1 matrix and the TA-2 matrix. All of the quartz-filled matrices were heated for one hour.

Table 3.3-4 shows property data for the dried and heated matrices. Heating produced little or no dimensional changes beyond those caused by drying. The TA-1 matrix re-wet to only 84% in water

DIMENSIONAL CHANGES WITH TIME IN 100% H₃PO₄ AT 150°C
(Dried Matrices)
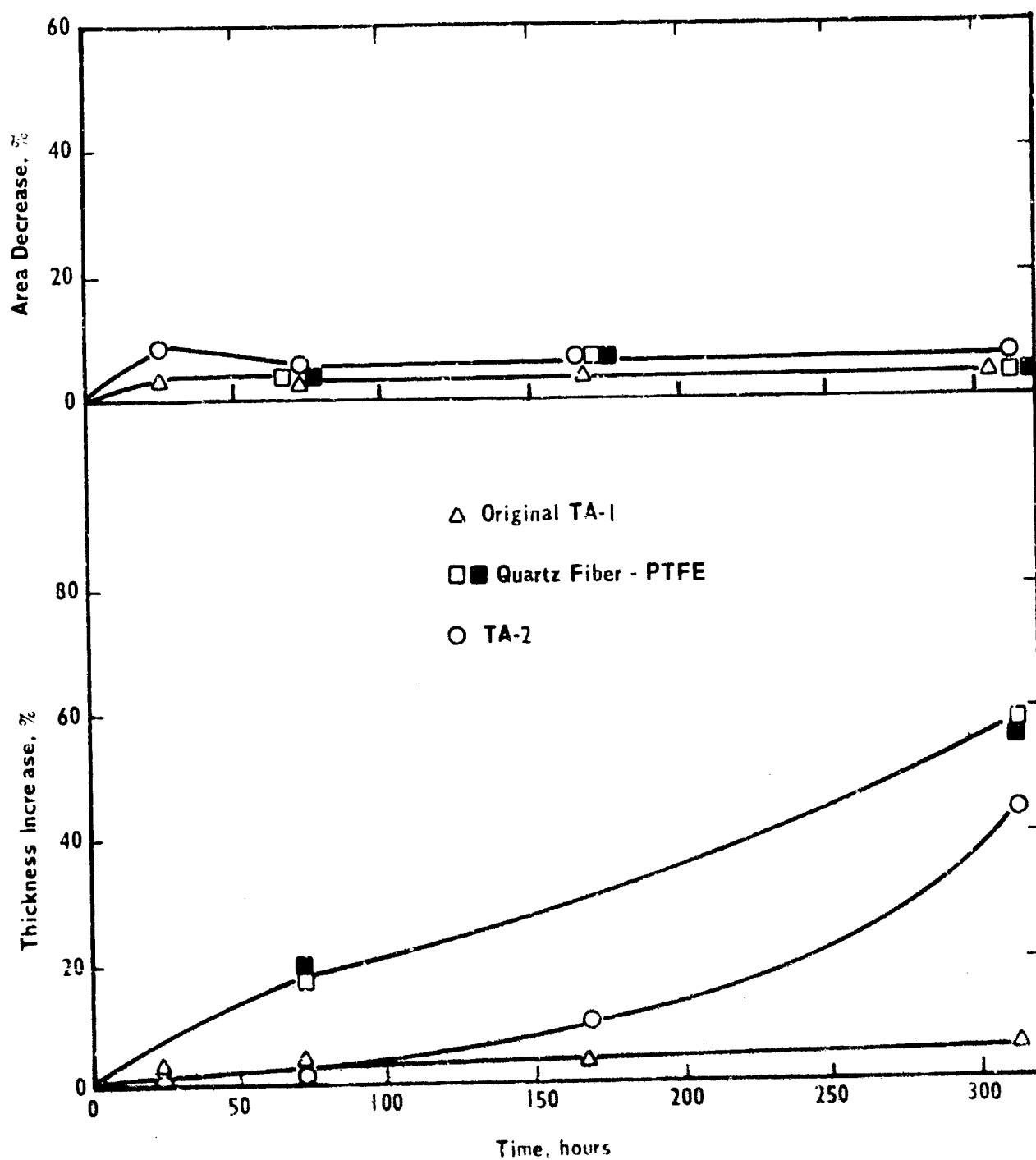
FIGURE 3.3-8

DIMENSIONAL CHANGES WITH TIME IN 100% H$_3$PO$_4$ AT 200°C
(Dried Matrices)

△ Original TA-1
○ TA-2
□ Quartz Fiber - PTFE
▨ ▧ Quartz Powder - PTFE
▽ Fine Quartz Powder - PTFE

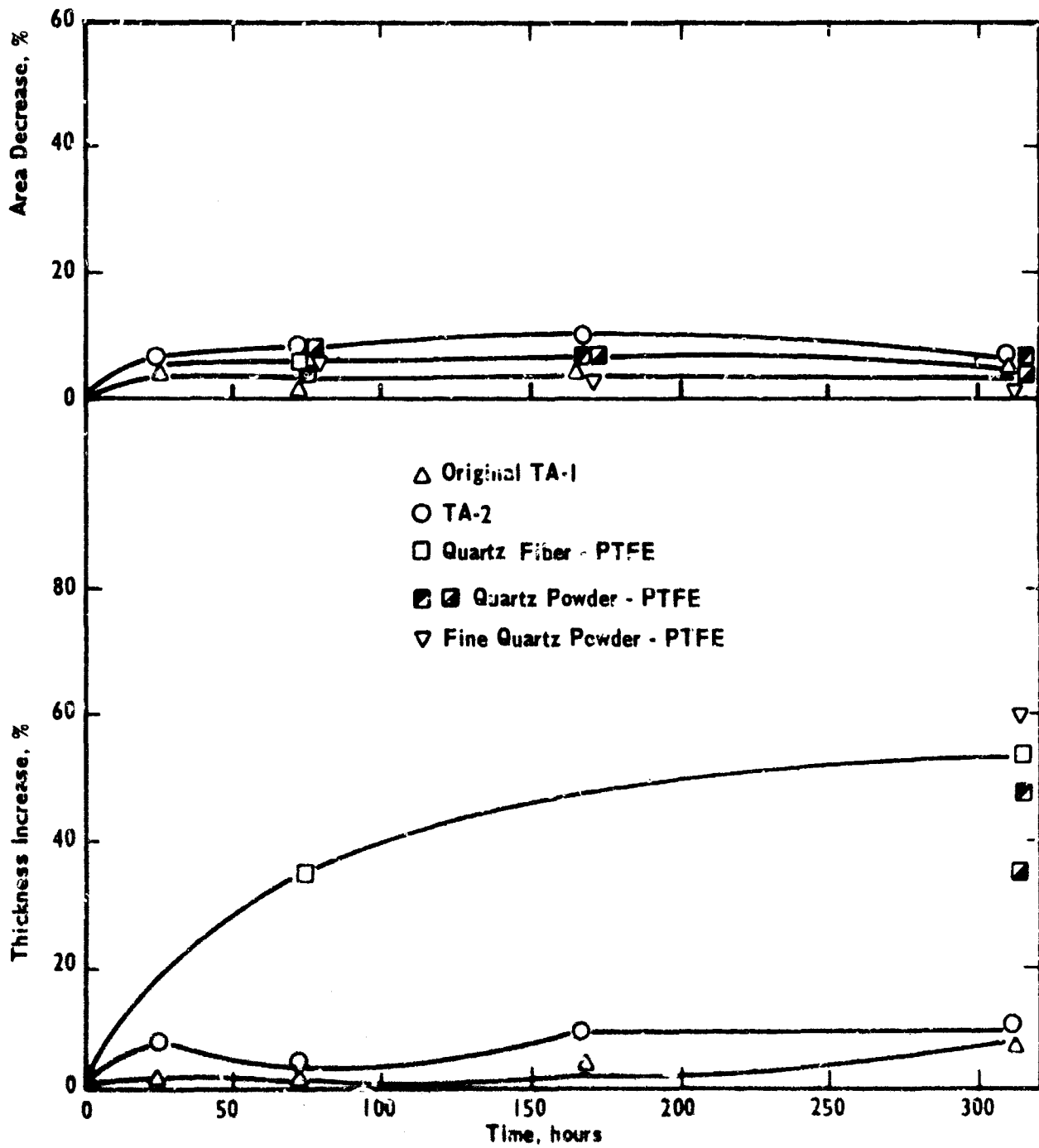FIGURE 3.3-9

DIMENSIONAL CHANGES WITH TIME IN 100% H_3PO_4 AT 150,200°C
(Dried and heated TA-1, TA-2 Matrices)

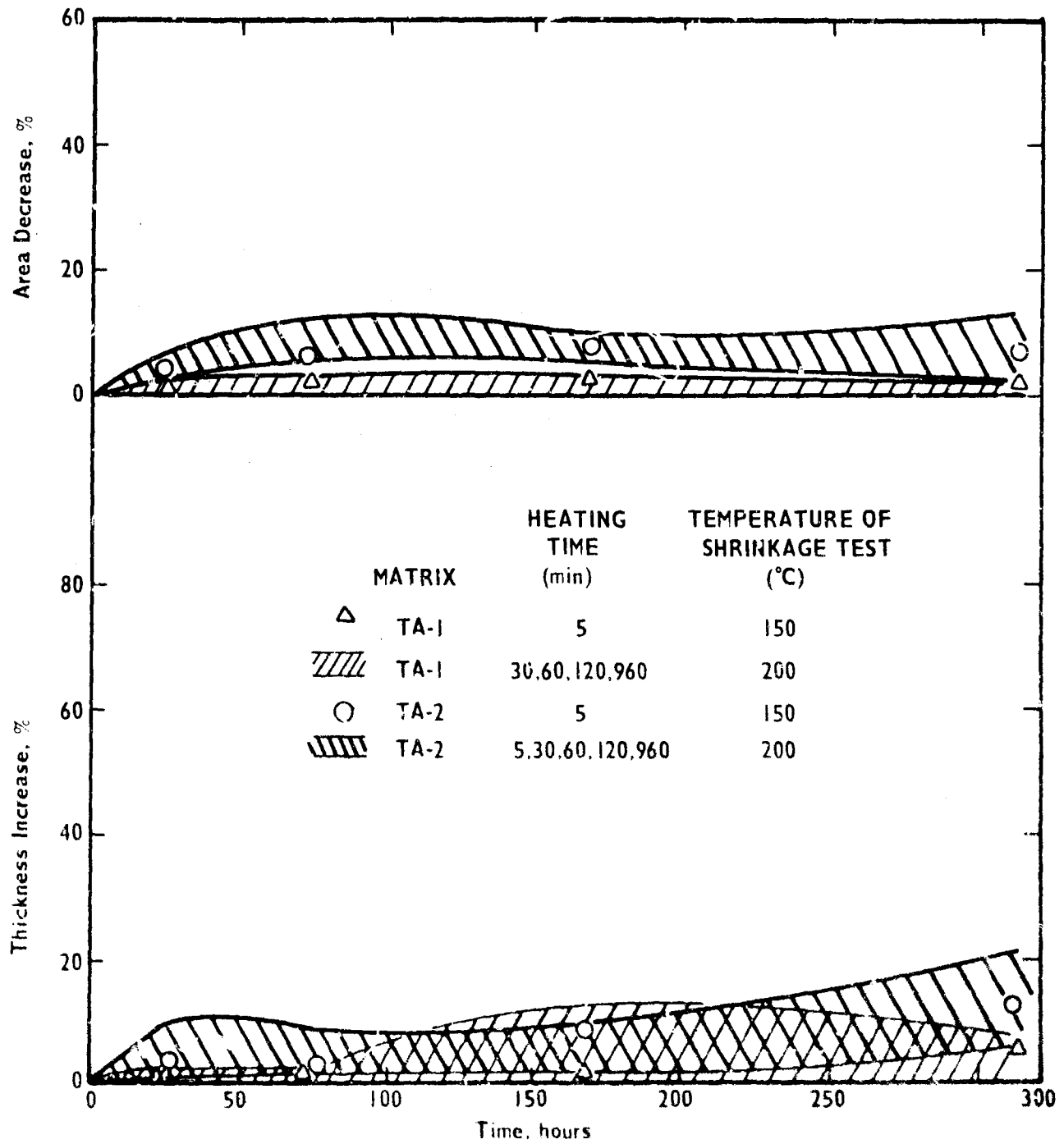|	MATRIX	HEATING TIME (min)	TEMPERATURE OF SHRINKAGE TEST (°C)
△	TA-1	5	150
▨	TA-1	30,60,120,960	200
○	TA-2	5	150
▨	TA-2	5,30,60,120,960	200

FIGURE 3.3-10

Table 2.1.4

Properties of Dried and Heated Matrices

Matrix Filler	Heated at 290-400°C [a]			Re-Wet [b]				Bubble [c] Pressure (psi)	Shrinkage in 100% H₃PO₄ [d]						Condition After Exposure at 150-200°C
	Change in		Porosity (%)	Water		85% H₃PO₄			150°C			200°C			
	Area (%)	Thickness (%)		Porosity (%)	Pore Volume Filled with Water (%)	Porosity (%)	Pore Volume Filled with Acid (%)		Change in		Porosity (%)	Change in		Porosity (%)	
									Area (%)	Thickness (%)		Area (%)	Thickness (%)		
PTFE Fiber (original TR-1)	-11	10	74	75/74	84/96	76	91	1.0	-2	6	72	0	5	75	Flexible
Zirconium Pyrophosphate Powder (TR-2)	-7	2	62	60	113	64	99	6	-7	13	64	-7	14	67	Flexible
Fine Quartz Powder	2	-1	54	52	100	55	100	6	-	-	-	1	70	73	Brittle & cracked
Quartz Powder	-3		55	56	91	56	90	1.5	-	-	-	-2	41	68	Brittle
Quartz Powder [e]	-1	1	63	63	82	62	92	0.7	-	-	-	1	75	75	Brittle
Quartz Fiber	-4	1	70	68	100	69	99	4	-	-	-	-3	69	81	Brittle & cracked

(a) Heated for 5 minutes to 16 hours.
(b) Re-wet under vacuum for 24 hours.
(c) Measured in water on one-inch diameter discs, at room temperature.
(d) Measured for 336 hours on two-inch diameter discs. Area and thickness changes based on dimensions of dried, heated, and rewet sample.
    Dimensional changes based on those of dried matrices.
    Pore volume is after 1/2 hours under vacuum.
    Porosity is after additional 16 hours.
    Compression at atmospheric pressure.
(e) Different thickness and porosity than other quartz powder-PTFE matrix.

after 2-1/2 hours of vacuum immersion, but additional immersion at atmospheric pressure for 16 hours produced nearly complete wetting. With the exception of one of the quartz powder matrices in water, all of the other matrices re-wet 90% or more after 2-4 hours' vacuum immersion. The limited data indicate that better re-wetting was obtained with the original TA-1 matrix in acid and with the TA-2 matrix in both water and acid than with corresponding dried matrices. Additional data are required to verify this effect. The dried and heated matrices generally have the same or slightly lower bubble pressures (1-2 psi lower) than the dried matrices.

Heating did not generally improve on drying in providing dimensional stability in acid at 150-200°C. Again, most of the dimensional changes occurred within the first 72 hours (Figures 3.3-10 and 11).

3.3.6.3 Dried and Sintered Matrices

Samples of dried matrices were free-sintered at 340-360°C and then cooled rapidly. Table 3.3-5 shows the resulting matrix properties.

Sintering the TA-1 matrix for 5 minutes to one hour caused considerable area loss (83%) and thickening (132%) as well as embrittlement. By contrast, all of the other filled-PTFE matrices, sintered for one hour, were dimensionally stable during this treatment. Among these, only the quartz powder matrices retained mechanical strength, however. The others (zirconium pyrophosphate, fine quartz powder, and quartz fiber) became too fragile to handle.
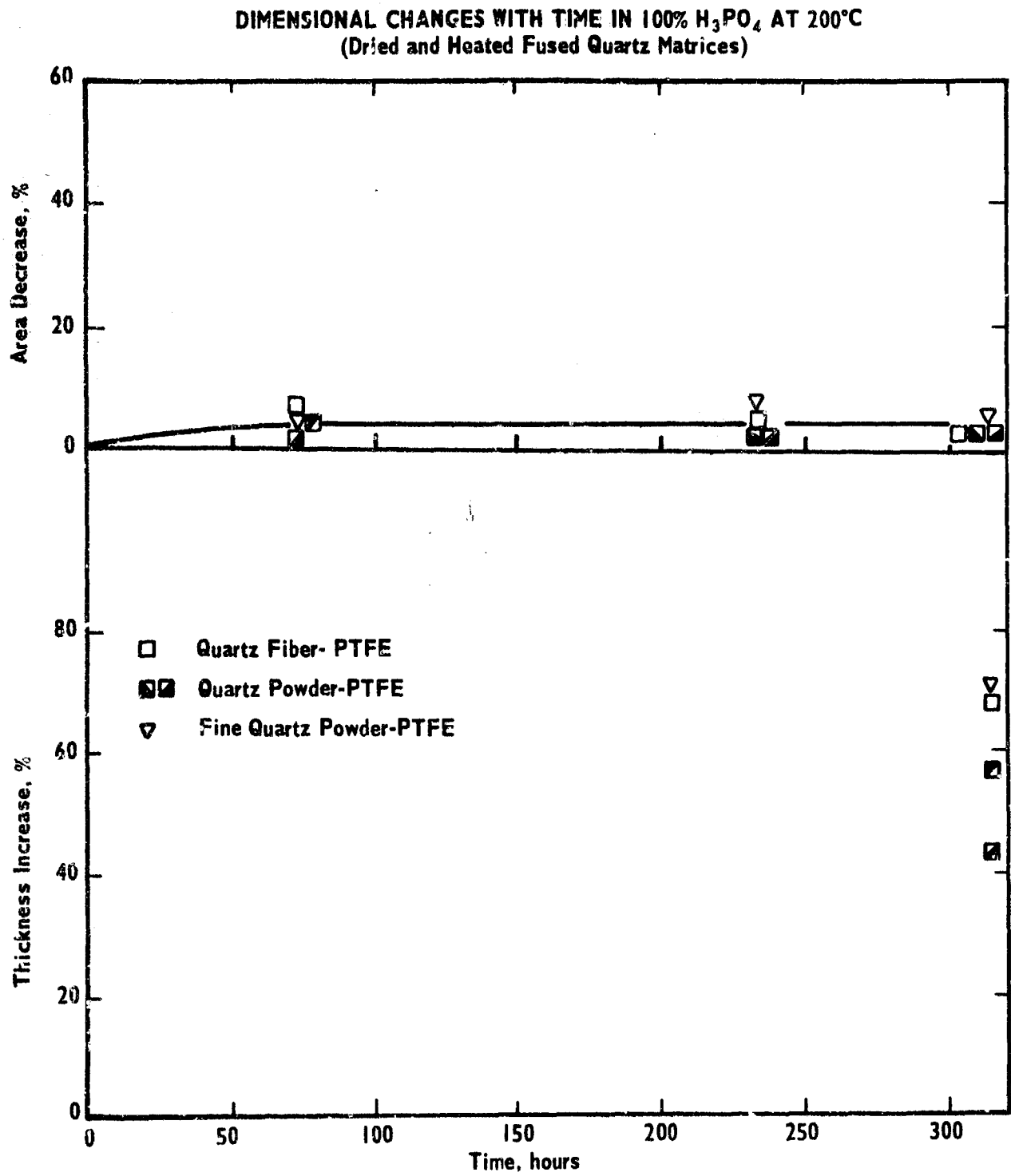
DIMENSIONAL CHANGES WITH TIME IN 100% H₃PO₄ AT 200°C
(Dried and Heated Fused Quartz Matrices)

FIGURE 3.3-11

Table 5.3.5

Properties of Dried and Sintered Matrices

Matrix Filler	Sintered at 340-360°C [a]				Re-Wet [b]					Shrinkage in 100% H_3PO_4 at 200°C [d]			
	Change in [e]		Porosity (%)	Mechanical Strength	Water		85% H_3PO_4		Bubble [c] Pressure (psi)	Change in		Porosity (%)	Condition
	Area (%)	Thickness (%)			Porosity (%)	Pore Volume Filled With Water (%)	Porosity (%)	Pore Volume Filled Wit. Acid (%)		Area (%)	Thickness (%)		
PTFE Fiber (Original TA-1)	-83	132	40	Brittle	-	-	-	-	-	-	-	-	-
Zirconium Pyrophosphate Powder (TA-2)	-1	1	62	Very fragile	-	-	-	-	-	-	-	-	-
Fine Quartz Powder	-	-	-	Very fragile	-	-	-	-	-	-	-	-	-
Quartz Powder	-2	2	56	Strong	56	90	57	93	0.2	0	20	66	Brittle
Quartz Powder [f]	-2	-4	60	Strong	62	90	64	102	0.5	2	54	77	Brittle
Quartz Fiber	0	3	69	Very fragile	-	-	-	-	-	-	-	-	-

(a) TA-1 heated 5 minutes to one hour. All others heated one hour.
(b) Re-wet under vacuum 24 hours.
(c) Measured in water on one-inch diameter discs, at room temperature.
(d) Measured for 310 hours on two-inch diameter discs. Area and thickness changes based on dimensions of dried, sintered, and re-wet sample.
(e) Dimensional changes based on those of dried matrices.
(f) Different thickness and porosity than other quartz powder-PTFE matrix.

The sintered quartz powder matrices re-wet well in water
and in acid. Compared to quartz powder matrices that were dried and
heated, they have lower bubble pressure in water, equally negligible
area loss and somewhat less thickening in hot acid at 150-200°C. Like
all of the quartz-filled matrices, regardless of post-treatment, they
embrittled in hot acid.

3.3.7 Life Test of Quartz-PTFE Matrix

A life test was run with an untreated quartz fiber-PTFE
matrix on H_2-air at 150°C and 100 mA/cm² (Figure 3.3-12). The maximum
voltage (0.695) was about the same as that obtained with the TA-1 matrix.
During 100 hours the cell resistance rose and the voltage declined rapidly.
These results are not surprising in light of the dimensional instability
of this form of the matrix and its embrittlement in the hot acid (Section
3.3.5).

3.3.8 Evaluation of Commercial Materials

3.3.8.1 Silica Cloth

Bubble pressures in water were measured on four grades of
a commercial silica cloth (Sil-Temp, made by Haveg Corporation) which
are 20-59 mils thick and 59-68% porous. All have negligible bubble
pressure (< 0.2 psi) and thus are unsuitable as matrices. The cloth
fiber, however, is of possible interest as a filler.

3.3.8.2 Tantalum Pentoxide Cloths

Tantalum pentoxide cloth No. 11 (Union Carbide Company),
described in Section 3.3.2.2, is 20-mil thick, 85% porous, and has
0.8-1.0 psi bubble pressure in water. The cloth broke when assembled
in a cell in the usual manner. The poor strength of this material and
its low bubble pressure make it unsuitable as a matrix.

LIFE TEST 252, QUARTZ-PTFE MATRIX
150°C, 95-100%H_3PO_4, H_2/Air
RA-2 Anode, AA-2 Cathode
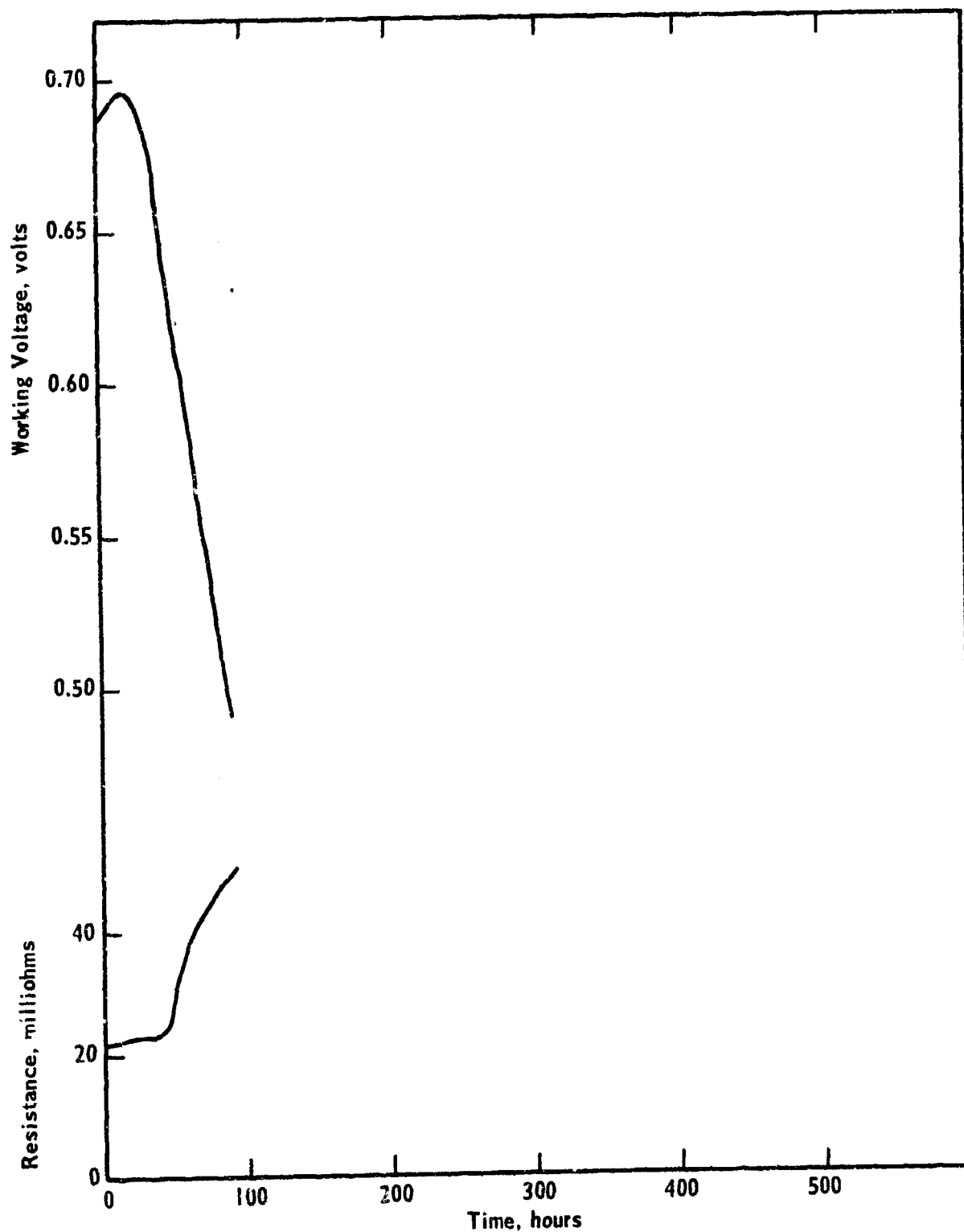Current Density: 100 ma/cm^2

FIGURE 3.3-12

Tantalum pentoxide cloth TC-100 (Union Carbide Company) made from the fiber described in Section 3.3.2.2 is 28 mils thick, 83% porous, and has about 1 psi bubble pressure in water. The cloth was first life tested on H_2-air at 100°C and 100 mA/cm^2 (Figure 3.3-13). Initial resistivity (0.4 ohm-cm^2) and voltage (0.66 V) were slightly better than that of the TA-1 matrix. Stable resistance and voltage were obtained for 350 hours at a voltage decline rate of 4.2 mV/100 hours. Raising the cell temperature to 150°C lowered the resistivity to 0.3 ohm-cm^2 and increased the voltage to 0.725 V. However, during the next 50 hours the voltage declined rapidly, with no resistance rise, because of a gas cross-leak. The low bubble pressure of this cloth makes it of doubtful use as a matrix.

3.4 Life Testing

All life tests run during this reporting period were operated at 100 mA/cm^2 with gas flows set at 1.5 x stoichiometric hydrogen and 3.0 x stoichiometric air. Standard TA-1 matrices (without drying or other modification) were used in all tests except a few which were set up specifically to evaluate experimental matrix materials. A summary of all life tests run during this period is shown in Table 3.4-1. Identification of electrodes and catalysts used is given in Table 3.4-2.

3.4.1 Long Term Hydrogen/Air Tests at 100, 150°C

Three extended duration life tests have been continued from previous reporting periods. Test 81 (AA-1 electrodes, 150°C) was terminated after 9,540 hours of operation when cross-leakage was observed. The condition of the cell components was similar to that noted in tests running 1,000 hours, but the effects were more pronounced. The anode spacer and catalyst support screens were severely embrittled. Some

LIFE TEST 244
TANTALUM PENTOXIDE CLOTH MATRIX (TC-100)
95-100% H_3PO_4, H_2/Air
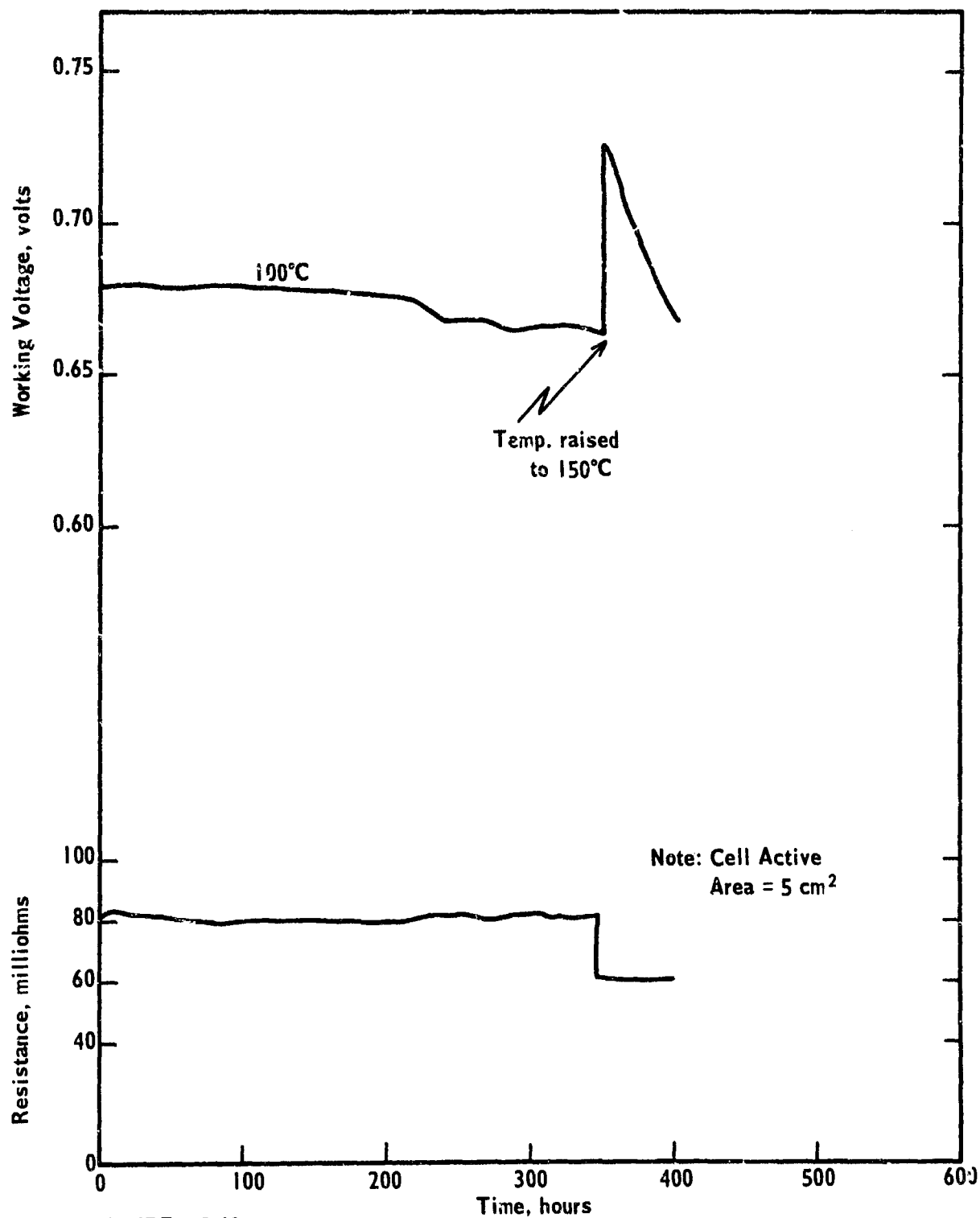**RA-2 Anode, AA-2 Cathode**
Current Density: 100 ma/cm^2

FIGURE 3.3-13

Table 3.4-1 Life Test Data [1]

Life Test Number	Anode	Cathode	Fuel Used [2]	Duration [3] (hrs.)	Performance Shown in Figure No.	Cell Voltage [3],[4] Max.	Cell Voltage Final	Cell Resistance, Milliohms Min.	Final	Comments
100°C Tests										
222	A4-3	A4-2	A,F	40	-	.551	.311	25	25	
226	A4-3	A4-2	A,F	353	-	.606	.596	16	17	
238	A4-3	A4-2	A	17	-	.325	.312	48	55	
95	A4-2	A4-1	A	(7100)	3.4-2	.663	(.600)	18	(26)	
126	A4-2	A4-1	A,B,C,D,G,H	696	3.4-15	.644	.641	20	23	
129	A4-2	A4-1	A	3185	3.4-15	.664	.619	20	24	
137	A4-2	A4-1	A	835	3.4-15	.645	.644	20	20	
142	A4-2	A4-1	A	142	-	.606	.606	22	31	Electrodes from test 140 reused
143	A4-2	A4-1	A	333	-	.630	.630	22	24	Cell reassembled with some electrodes but new matrix at 215, 292, 515 hrs.
				714		.663	.612	19		
150	A4-2	A4-2	A	138	3.4-15	.639	.637	22	22	
158	A4-2	A4-2	A	184	3.4-15	.603	.603	28	20	Excess electrolyte left on matrix surface (120% saturation)
159	A4-2	A4-2	A,B	568	-	.637	.635	18	18	
160	A4-2	A4-2	A,B,C,D	1360	3.4-15	.660	.649	21	21	Electrodes washed with 30% H_2SO_4 before use
166	A4-2	A4-2	A	640	3.4-15	.658	.657	21	21	
178	A4-2	A4-2	A	20		.485	.473	24	24	
188	A4-2	A4-2	A	65	3.4-15	.582	.578	41	41	
190	A4-2	A4-2	A	210	3.4-15	.615	.277	20	20	
196	A4-2	A4-2	A	132	3.4-15	.530	.490	20	20	
198	A4-2	A4-2	A,F	1846	3.4-16	.668	.566 (F)	18	16	
202	A4-2	A4-2	A,F	713	3.4-15	.634	.633	16	42	
212	A4-2	A4-2	A	88	-	.569	.538	42	30	
214	A4-2	A4-2	A,F	80	3.4-16	.479	.479	30	(16)	
224	A4-2	A4-2	A,F	(1298)	3.4-16	.664	(.592)(F)	16	20	
				1054		.649	.575 (F)	19		
210	A4-2	A4-2(H)	A,F	19	-	.565	.562	19	19	O_2 over anode, H_2 over cathode at 100°C during startup
228	A4-2	A4-2(H)	A,F	235	-	.640	.412 (F)	20	20	O_2 over anode, H_2 over cathode at 150°C during startup
232	A4-2	A4-2(H)	A,F	789	-	.654	.524 (F)	18	19	
242	A4-2(H)	A4-2	A,F	(668)	3.4-16	.582	(.532)(F)	16	(18)	
125°C Tests										
169	A4-2	A4-2	A,B	790	-	.676	.654 [5]	22	22	Temperature raised to 150°C at 570 hrs.
150°C Tests										
61	A4-1	A4-1	A	9540	3.4-2	.683	.384	16	55	
138	A4-3	A4-1	A,B	670	-	.686	.369 (B)	23	38	
213	A4-2	A4-2	A,E	571	3.4-9	.717	.685	14	16	
215	A4-2	A4-2	A,E	230	-	.665	.536	17	18	
219	A4-3	A4-2	A,E	1196	3.4-9	.715	.633	17	22	Electrode surface dusted with graphite

- 65 -

Table 2.6-1 Life Test Data (1) (Continued)

Cell Voltage (3),(4)		Cell Resistance, Milliohms		Comments
Max.	Final	Min.	Final	

Performance Shown in Figure No.

Cell Voltage Max.	Final	Res. Min.	Final	Comments
.708(6)	(.503)(6)	13	(41)	Test run on O₂
.781(6)	.752(6)	21	23	Electrodes from test 106 (480 hrs. at 100°C) reused
.615	.613	20	22	Electrodes from test 108 (1106 hrs. at 100°C) reused
.689	.390(8)	21	22	Cathode from test 108 (1842 hrs. at 100°C) reused
.656	.639	16	32	Cathode from test 108 (1842 hrs. at 100°C) reused
.642	.598	28	32	Cathode from test 119 (690 hrs. at 100°C) reused
.674	.646	18	24	
.684	.630	28	25	
.682	.014(8)(6)	24	38	Cell run on O₂ after 240 hrs.
.697	.740(8)	24	33	Cell run on O₂ after 376 hrs.
.674	.671(8)	30	51	Cell run on O₂ after 260 hrs.
.712	.694(6)	12	48	Cell run on O₂ after 60 hrs.
.592	.532	25	25	Electrodes prewet with 85% H₃PO₄
.709	.575	24	32	Fuel B at 3x and 1.5x stoichiometric H₂
.634	.534	42	42	Anode prewet with 85% H₃PO₄
.710	.484	19	54	Fuel E at 3x and 1.5x stoichiometric H₂
.781(6)	.699(6)	24	33	Test run on O₂
.621	.421	33	36	Cathode prewet with 85% H₃PO₄
.688	.478(8)	21	45	Electrodes leached 3.5 days in 85% H₃PO₄ at room temperature
.704	.010	26	21	
.717	.082	28	27	Cathode leached 4 days in 85% H₃PO₄ at 100°C
.679	.079	27	23	Glass Fiber Matrix
.670	.670	24	28	H₃PO₄ saturated matrix heated 4 days at 150°C
.688	.655	26	26	Matrix heated 7 days at 100°C in excess H₃PO₄
.683	.618	22	28	Matrix treated same as in test 189
.724	.540(8)	17	23	Cell reassembled with same electrodes but new matrix at 42, 90 hrs.
.712	.450	22	26	
.688	.455	33	28	
.724	.572	19	21	Modified cell design ("serpentine" gas flow)
.686	.076	23	20	Cathode leached 5 days in 85% H₃PO₄ at 100°C. Fuel E at 3x and 1.5x stoichiometric H₂
.99	.063	15	22	Electrode surface dusted with Baymal
.698	.058	24	19	
.705	.042(8)(7)	14	19	Electrode surface dusted with graphite. Temperature raised to 100°C ... hrs.
.722	.180(8)	19	24	Electrode surface dusted with graphite. O₂ over anode during start
.710	.06	13	18	Electrode surface dusted with graphite
.728	.180	19	21	Cell held 24 hrs. at 150°C before startup
.720	.95	25	21	Cell held 4 days at 150°C before startup
.727	.015	28	40	O₂ over anode during startup
.727	.020(8)	15	22	O₂ over anode during startup
.712	(.146)	15	23	Cell held 2.5 days at 150°C before startup
.702	.089	17	20	Cell held 2.5 days at 150°C before startup

Table 3.4-1 Life Test Data[1] (continued)

Life Test Number	Anode	Cathode	Fuel Used[2]	Duration[G] (hrs.)	Performance Shown in Figure No.	Cell Voltage[3],[4] Max.	Cell Voltage[3],[4] Final	Cell Resistance, Milliohms Min.	Cell Resistance, Milliohms Final	Comments
	RA-2	AA-2	A,E	330	3.4-5,7	.703	.662	16	21	
	RA-2	AA-2	A,E	117	-	.673	.375(E)	12	16	
	RA-2	AA-2	A,E	<1	-	.689	.614	-	190	Tantalum Oxide Cloth #11 Matrix
	RA-2	AA-2	A,E	351	3.4-5,7	.710	.609(E)	13	13(8)	Tantalum Oxide Cloth TC-100 Matrix. Run in 1" cell
	RA-2	AA-2	A,E	400	3.3-13	.726	.040	66	48(8)	
	RA-2	AA-2	A,E	(236)	3.4-5	.693	.652	13	16	O_2 over anode, H_2 over cathode during startup
	RA-2	AA-2	A	(233)	3.4-6,14	.731	(.655)(E)	15	(20)	Experimental quartz fiber - PTFE matrix
	RA-2	AA-2	A	116	3.3-12	.695	.359	22	85	
	RA-2	AA-2(M)	A,E,G	616	3.4-5	.718	.504(E)	14	20	
	RA-2	AA-2(M)	A,E	258	3.4-6,7	.712	.666(E)	16	17	O_2 over anode, H_2 over cathode during startup
	RA-2	AA-2(M)	A,E,G	116	-	.693	.685	16	16	
	RA-2	AA-2(M)	A,E	673	-	.704	.676	15	19	
	RA-2	AA-2(M)	A,E	93	3.4-7	.697	.559(E)	19	18	O_2 over anode, H_2 over cathode during startup
	AA-2(M)	AA-2	A,E	(834)	3.4-8	.703	(.645)(E)	14	(16)	
	AA-2(M)	AA-2	A,E	500	3.4-8	.701	.654	15	15	
	AA-2(M)	AA-2	A,E	24	-	.669	.590(E)	17	17	
	AA-2(M)	AA-2	A,E	(617)	3.4-8,14	.707(E)	(.590)(E)	14	(20)	
	RA-2(M)	AA-2(M)	A,E	(763)	3.4-8	.764	(.652)(E)	14	(17)	
	AA-3(A)	AA-2(M)	A,E	(738)	3.4-9	.694	(.625)(E)	16	(18)	
	AA-2(M)	AA-2	A,E	379	3.4-9	.707	.600(E)	14	23	
	AA-2(M)	AA-2(M)	A	(92)	3.4-7	.738	(.708)	13	(13)	
	RA-2	AA (Pt Screen)	A	1312	3.4-11	.685	.633	13	15	
	RA-2	AA	A	930	3.4-13	.585	.555	17	18	
	RA-2	AA-3	A	474	3.4-12	.714	.664	18	21	
	RA-2	AA	A	184	3.4-13	.571	.548	20	20	
	RA-2	AA (Pt Screen)	A	16	-	.422	.422	22	27	
	RA-2	AA	A	308	3.4-11	.669	.637	11	17	
	RA-2	AA	A	592	3.4-11	.696	.656	13	16	
	AA-2	AA	A	471	3.4-13	.554	.514	13	15	
	RA-2	AA	A	1000	3.4-12	.514	.615	24	24	
	RA-2	AA	A	113	-	.571	.564	44	44	
	RA-2	AA	A	42	-	.282	.203	18	17	
	RA-2	AA	A	305	3.4-12	.622	.595	18	18	
	RA-2	AA	A	280	-	.487	.448	18	16	
	RA-2	AA	A	162	3.4-13	.633	.597	16	16	
	RA-2	AA	A	13	-	.349	.349	48	69	Cell run on O_2 from 646 to 855 hrs.
	RA-2	AA	A	<1	-	-	-	-	-	
	RA-2	AA	A	114	3.4-12	.612	.591	13	13	
	RA-2	AA	A	347	3.4-13	.595	.323	17	19	
	RA-2	AA	A	160	3.4-13	.585	.503	21	26	
	RA-2(M)	AA	A,E	(284)	3.4-7,12	.675	(.596)(E)	12	(14)	
	AA-2	AA	A	163	3.4-13	.647	.272	14	-	
	RA-2,M	AA	A,E	166	3.4-13	.587	.576	15	15	

Table 3.4-1 Life Test Data [1] (Continued)

Life Test Number	Anode	Cathode	Fuel Used [2]	Duration [3] (hrs.)	Performance shown in Figure No.	Cell Voltage [3],[4] Max.	Cell Voltage [3],[4] Final	Cell Resistance, Milliohms Min	Cell Resistance, Milliohms Final	Comments
136	BA	AA-1	A,B	456	3.4-10	.688	.548(B)	20	25	
131	BA	AA-1	A,B	310	3.4-10	.698	.656	17	22	
136	BA	AA-1	A,B	325	3.4-10	.703	.390(B)	20	28	
157	EA	AA-2	A,B	1,507	3.4-10	.703	.638	21	29	
187	EA	AA-2	A,B	188	3.4-10	.700	.496(3)	18	21	
192	A	AA-2	A	85	-	.467	.390	99	105	
236	AA	BA	A,E	(784)	3.4-9,12	.684	(.617)(E)	14	(18)	

Notes:

(1) All tests were run at 100 ma/cm² in 2" x 2" active area cells, with TA-1 matrix initially saturated in 85% H_3PO_4, and air at the cathode unless otherwise noted. For details with respect to the electrodes used in each test, see Table 3.4-2.

(2) Fuel used:
A: Pure H_2
B: 90% H_2, 10% CO
C: 97% H_2, 3% CO
D: 99% H_2, 1% CO
E: 70% H_2, 3% CO, 27% CO_2
F: 70% H_2, 1% CO, 29% CO_2
G: 70% H_2, 30% N_2
H: 70% H_2, 30% CO_2

Fuel rate 1.5x stoichiometric H_2 unless otherwise noted

(3) For continuing tests, data as of 1/15/68 are shown in parenthesis

(4) Letter in parenthesis indicates test fuel if other than pure H_2 (see note 2)

(5) At 150°C

(6) Voltage on H_2/O_2

(7) At 165°C

(8) One-inch (5 cm²) active area cell

Table 3.4-2 Life Test Electrode and Catalyst Identification

Table 1xx-2 Life Test Electrode and Catalyst Identification (Continued)

- 69 -

Cathode

Anode

Table 3.4-2 Life Test Electrode and Catalyst Identification (Continued)

Life Test Number	Anode							Cathode						
	Type	Noble(1) Metal mg/cm²	Cyanamid Graphite mg/cm²	Wt.% PTFE	Electrode Sheet No.	Catalyst No.	Comment	Type	Noble(2) Metal mg/cm²	Cyanamid Graphite mg/cm²	Wt.% PTFE	Electrode Sheet No.	Catalyst No.	Comment
234	RA-2	5	5	25	MH-559-6B	88362-1444		AA-2	10	--	35	88333-150-2	14,063	
237	RA-2	5	5	25	MH-559-7A	88362-1444		AA-2	10	--	35	88333-150-2	14,063	
244	RA-2	5	5	25	LD213-548-C	88362-11-3		AA-2	10	--	35	88333-150-1	14,063	
249	RA-2	5	5	25	SBC33-170	88362-42-12		AA-2	10	--	35	88333-164-1	14,063	
251	RA-2	5	5	25	SB333-170	88362-42-12		AA-2	10	--	35	88333-164-1	14,063	
252	RA-2	5	5	20	MH-559-8A	88362-1444		AA-2	10	--	35	88333-167-2	14,063	
226	RA-2	5	5	25	MH-559-7B	C8362-1444		AA-2(X)	25	--	35	88333-145	14,063	Secondary extractable filler used
227	RA-C	5	5	25	MH-559-7A	88362-1444		AA-2(X)	25	--	35	88333-151	14,063	
229	RA-2	5	5	25	MH-559-7A	88362-1444		AA-2(X)	10	--	35	88333-151	14,063	
230	RA-2	5	5	25	MH-559-6B	88362-1444		AA-2(X)	10	--	35	88333-151	14,063	
235	RA-2	5	5	25	MH-559-7A	88362-1444		AA-2(X)	10	--	35	88333-151	14,063	
233	RA-2(X)	5	5	25	88333-160	87835-29-7	Secondary extractable filler used	AA-2	10	--	35	88333-150-2	14,063	Secondary extractable filler used
240	RA-2(X)	5	5	25	88333-168	78362-42-12		AA-2	10	--	35	88333-150-2	14,063	
243	RA-2(X)	5	5	25	88333-168	88362-42-12		AA-2	10	--	35	88333-167-1	14,063	
245	RA-2(X)	5	5	25	88333-168	88362-42-12		AA-2	10	--	35	88333-167-1	14,063	
239	RA-2(X)	5	5	25	88333-160	87835-29-7	Secondary extractable filler used	AA-2(X)	10	--	35	88333-151	14,063	Secondary extractable filler used
241	RA	5	7	25	88333-96	87835-29-7	No graphite added	AA-2(X)	10	--	35	88333-151	14,063	
253	RA-3	5	5	25	88333-173	87835-29-7		AA-2	10	--	35	LD213-164-1	14,063	
255	RA-2(X)	5	5	25	88333-171	87835-29-7	Secondary extractable filler used	AA-2(M)	10	--	35	88333-172	14,063	Secondary extractable filler used
124	RA-2	5	5	25	LD213-504-12B	88362-11-3		AA	10	7.5	25	87971-110	--	Platinum support screen 7.5% Pt on graphite
134	RA-2	5	5	25	LD213-50-4B	J7835-48-10		RA	5	7.5	25	87971-105-2	87669-132-00	Physical mix, Pt black + graphite
144	RA-2	5	5	25	LD213-551-12B	88362-11-3		RA	5	7.5	35	87510-158-2	--	
147	RA-2	5	5	25	LD213-551-12B	88362-11-3		AA-3	5	7.5	25	88110-26-10	--	matrix side } Pt-sliver electrode
152	RA-2	5	5	25	LD213-551-12B	88362-11-3		RA	10	--	40	87971-107-2	--	gas side } Pt screen extracted with HF
154	RA-2	5	5	25	LD213-551-12B	88362-11-3		AA-1	10	--	15	87971-106-1	--	Platinum support screen
155	RA-2	5	5	25	LD213-551-12B	88362-11-3		RA	10	--	25	88333-92	--	7.5 Pt on graphite
156	RA-2	5	5	25	LD213-551-12D	88362-11-3		RA	10	--	25	88333-85	37.0-132-00	
163	RA-2	5	5	25	LD213-504-15B	87835-41-11		RA	10	--	25	87971-104-2	874.9-132-00	
170	RA-2	5	5	25	MH-559-5B	88362-11-4		RA	5	--	35	88333-109	--	matrix side } evacuated electrode gas side
172	RA-2	5	5	25	MH-559-5B	58362-1444		BA	2.5	2.5(?)	35	88333-117-2	88513-00	2.5% Pt in Pd-Co
174	RA-2	5	5	25	MH-559-5B	88362-1444		RA	10	10	35	RA333-124	87459-132-00	7.5% Pt on graphite
176	RA-2	5	5	25	MH-559-5B	88362-1444		RA	5	7.5(?)	35	88333-110	88535-34	7.5 Pt, 7.5 Rh on graphite
180	RA-2	5	5	25	MH-559-5B	88362-1444		BA	2.5	7.5(?)	25	88333-127	87719-10	7.5 Pt on graphite
180A	RA-2	5	5	25	MH-559-5B	88362-1444		BA	2.5	7.5(?)	25	88333-107-1	88533-63	2.5% Pt on Pd-Co
182	RA-2	5	5	25	MH-559-5B	88362-1444		B:	10	--	35	88333-128	--	matrix side } Pd-sliver electrode gas side
184	RA-2	5	5	25	MH-559-5B	88362-1444		RA	10	10	15	RA333-132	86459-132-00	7.5% Pt on graphite
185	RA-2	5	5	25	MH-559-5B	88362-1444		RA	5	--	35	88333-127	87719-10	
246	RA-2	5	5	25	MH-559-2B	88362-1444		RA	5	--	35	88333-169	--	Physical mix, Pt black + graphite

Table 3.4-2 Life Test Electrode and Catalyst Identification (Continued)

Life Test Number	Anode							Cathode						
	Type	Noble(1) Metal mg/cm²	Cyanamid Graphite mg/cm²	Wt.% PTFE	Electrode Sheet No.	Catalyst No.	Comment	Type	Noble(2) Metal mg/cm²	Cyanamid Graphite mg/cm²	Wt.% PTFE	Electrode Sheet No.	Catalyst	Comment
247	RA-2(W)	5	5	25	88362-168	88362-42-12		BA	10	10	25	87971-104-2	87669-132-66	50% Pt on graphite
250	RA-2	5	5	25	MA-559-8A	88362-14-4		BA	5	7.5	25	88114-174	87669-148-74	25% Pt on graphite, + Pt black
257	RA-2(W)	5	5	25	88333-160	87835-29-7		BA	5	5	35	88133-179	87669-132-46	50% Pt on graphite
130	BA	5 Pt	5	25	87971-106-2	87669-132-46	50% Pt on graphite	AA-1	10	-	35	87971-104-2	14,06J	
131	BA	2.5 Pt, 2.5 Ru	5	25	87971-93-1	88358-58	25% Pt, 25% Ru on graphite	AA-1	10	-	45	87971-104-1	14,06J	
136	BA	2.5 Pt, 2.5 Rh	5	25	88110-24-2	87719-192, 88108-98	25% Pt, 25% Rh on graphite	AA-1	10	-	35	87971-104-1	14,06J	
157	BA	5 Pt	5	35	88333-65	87669-132-46	50% Pt on graphite	AA-2	10	-	45	88113-81-2	-	
187	PA	2.5 Pt, 2.5 Ru	5	35	88333-94	88358-146	25% Pt, 25% Ru on graphite	AA-2	10	-	45	88113-81-1	-	
192	BA	2.5 Pt	7.5(3)	23	88333-107-1	88535-60	25% Pt on Darco G-60	AA-2	10	-	35	88113-136-1	14,06J	
236	BA	5 Pt	5	25	87971-106-2	87669-132-46	50% Pt on graphite	BA	10	10	25	87771-104-2	87669-132-66	50% Pt on graphite

Notes:

(1) 1:1 Pt:Rh unless otherwise noted

(2) Pt unless otherwise noted

(3) Darco G-60 used as a support in place of Cyanamid Graphite

blanking of the TA-1 matrix occurred on the air side in the area between the electrode edges and the inner edge of the cell gasket. The anode adhered to the matrix surface but could be separated by soaking in water. White globules of amorphous material were found in the gas spaces of both sides of the cell, on the back of the electrodes, in the spacer screens, and on the cell plates. Efforts to identify this material have not been successful. Traces of these deposits can be seen in Figure 3.4-1 as white spots on the gas side of the anode.

For the first 5,000 hours of operation, Test 81 ran with only a moderate decline (see Table 3.4-3 and Figure 3.4-2) but with decreasing stability thereafter. The voltage decline of Test 110, running with an RA-2 anode, has been more rapid and is associated with an earlier increase in cell resistance. The best voltage level after 7,000 hours' elapsed time was exhibited in Test 95 (RA-2 anode, AA-1 cathode, 100°C), indicating greater stability for tests operating at this lower temperature. Tests 110 and 95 are continuing.

3.4.2 Tests at 150°C

Hydrogen/air performance for RA-2 anode/AA-2 cathode cells was evaluated during the previous reporting period.[2-b] Testing with a 10% CO/90% hydrogen fuel mixture, begun in the last period, was continued during the early portion of this period. Later tests at 150°C were carried out with a synthetic reformate containing 3% CO, 27% CO_2, and 70% H_2.

3.4.2.1 Standard (RA-2) Anodes and (AA-2) Cathodes

3.4.2.1.1 Performance with 10% CO/90% H_2 Fuel

The cell response to the change in fuels from H_2 to H_2 with 10% CO has been evaluated throughout the course of several life

AA-1 ELECTRODES AFTER 9540 HOUR LIFE TEST (81)
150°C, 95-100% H_3PO_4, H_2/Air, 100 ma/cm^2
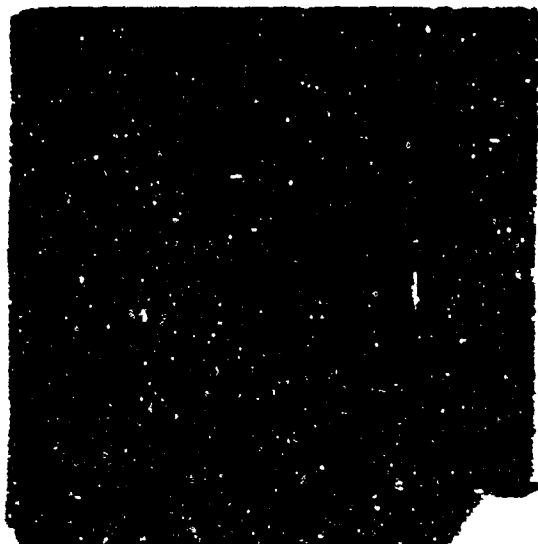
Anode, matrix side
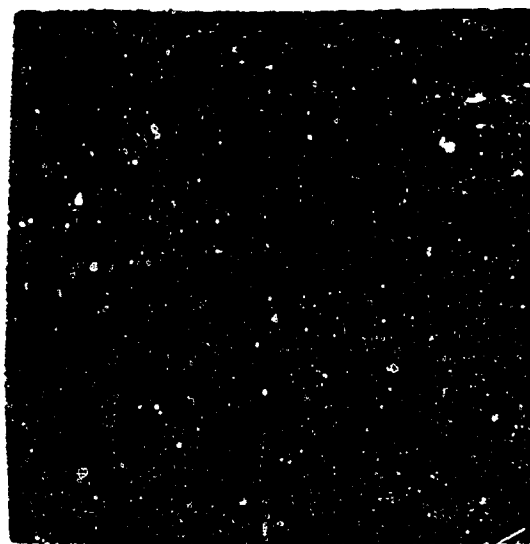
Cathode, matrix side
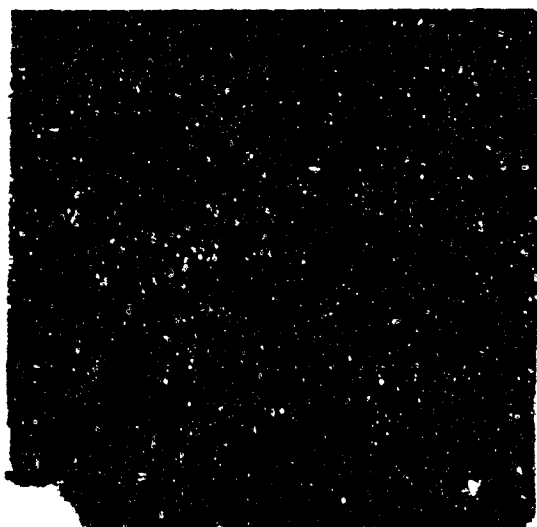
Anode, Gas Side
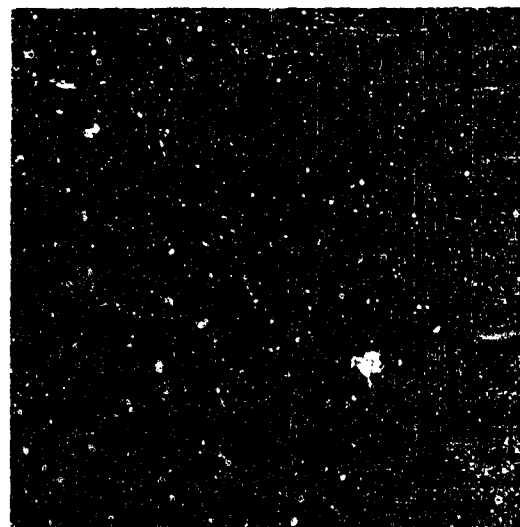
Cathode, gas side

FIGURE 3.4-1

Table 3.4-3

Long Term H₂/Air Tests

Life Test Number	Temp. °C	Anode	Cathode	Current Density ma/cm²
81	150	AA-1	AA-1	100
95	100	RA-2	AA-1	100
110	150	RA-2	AA-1	100

Elapsed Time (hours)	Rate of Voltage Decline (mV/100 hrs.)			Rate of Resistance Rise (milliohms/1,000 hrs.)		
	Test 81	Test 95	Test 110	Test 81	Test 95	Test 110
0-1000	4	*	7	1.6	0	3.0
1000-2000	2	*	4.3	1.6	1.0	4.0
2000-3000	0.7	0.8	0.8	1.6	1.3	4.0
3000-5000	0.7	0.8	3.9	1.6	1.3	8.5
5000-8000	2.5	0.8	1.8	6	1.3	1.0
8000-9000	7.5	-	-	9	-	-
9000-9540	Accelerating	-	-	Accelerating	-	-

* Voltage rising during this period

LONG TERM HYDROGEN/AIR LIFE TESTS
Current Density: 100 ma/cm²

TEST NO.	TEMP., °C	ANODE	CATHODE
81	150	AA-1	AA-1
95	100	RA-2	AA-1
110	150	RA-2	AA-1
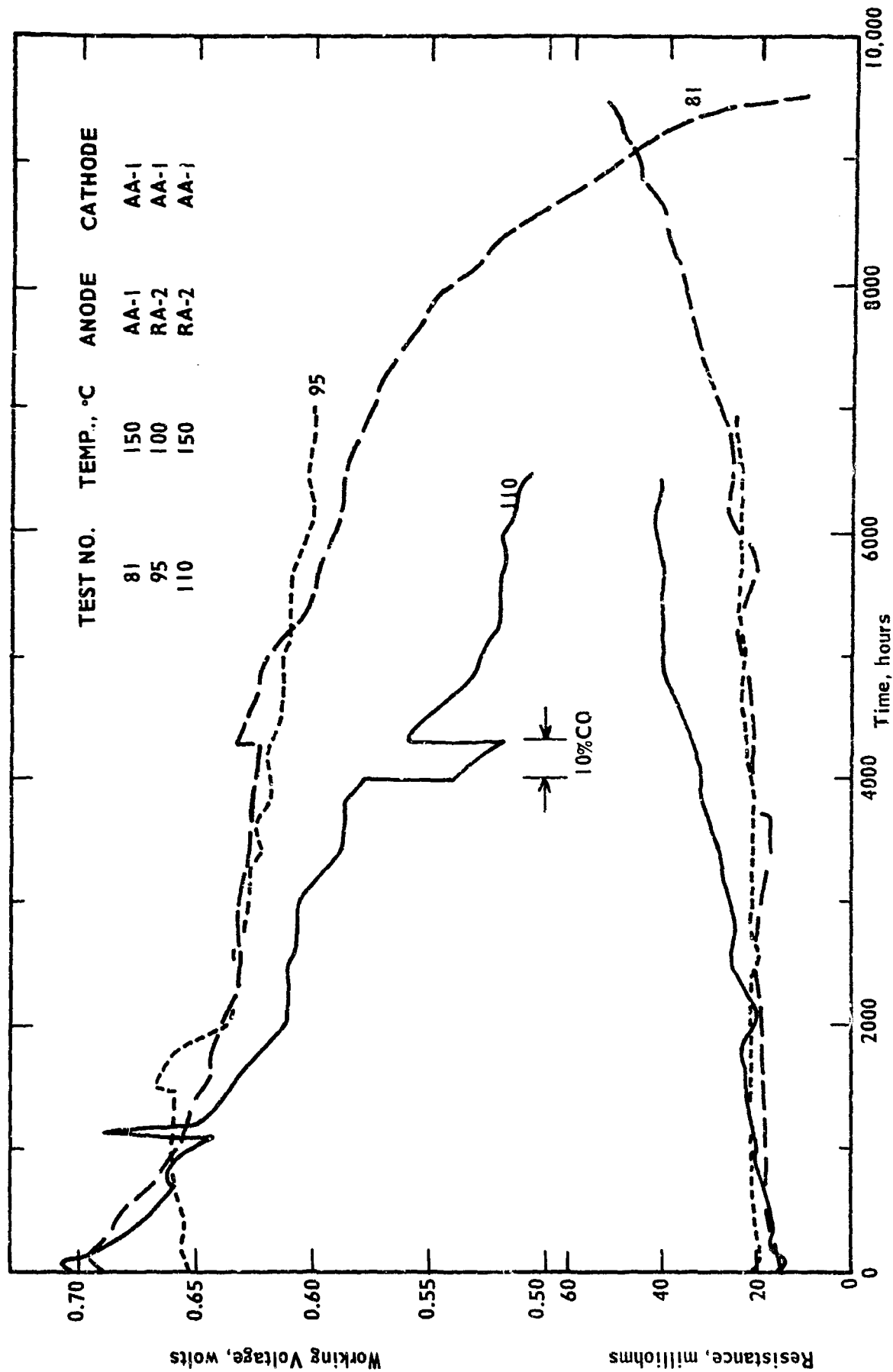
FIGURE 3.4-2

tests and is shown in Figure 3.4-3. The connected points indicate data obtained on the same test. Response to CO appears to be increasing from about 20 mV initially to about 50-90 mV after 1,000-1,200 hours. This suggests that anode stability on 10% CO is not as great as on H_2. However, in Test 110 a response of only 40-50 mV was observed after 4,000 hours of operation.

Extended periods of operation with the 10% CO fuel mixture for several tests are shown in Figure 3.4-4. The initial point of each curve is the hydrogen/air performance immediately prior to switching to the 10% CO fuel mixture. The voltage stability in these tests appears to be comparable (12-15 mV loss/100 hours) to tests on H_2 during the first 500 hours. However, during the second 500 hours, the tests on 10% CO continued to decline at 12-15 mV/100 hours whereas the decline rate on pure H_2 decreased to about 4-9 mV/100 hours.

3.4.2.1.2 Performance with Synthetic Reformate (3% CO/27% CO_2/70% H_2)

Previous polarization work[2-c] at 150°C indicated that at 100 mA/cm^2, RA-2 anodes could be expected to lose approximately 30 mV when switched from pure hydrogen to synthetic reformate. Early life-test results were much poorer, however, with initial performance losses ranging from 47 to 120 mV, and high decline rates. Performance curves are shown in Figure 3.4-5. Initial points are H_2/air performance immediately prior to switching to synthetic reformate.

Subsequently it was found that the performance of the RA-2 anodes could apparently be improved by an "oxygen treatment" carried out during start-up or a "gas reversal treatment" during the course of the run. Start-up treatment consisted of heating the cell to operating temperature (150°C) and then passing oxygen over the anode and (in some cases) hydrogen over the cathode for periods of 10-30 minutes. The cell

RA-2 ANODES: RESPONSE TO 10%CO/90%H$_2$, (150°C)
95-100%H$_3$PO$_4$, 100 ma/cm^2

Time, hours

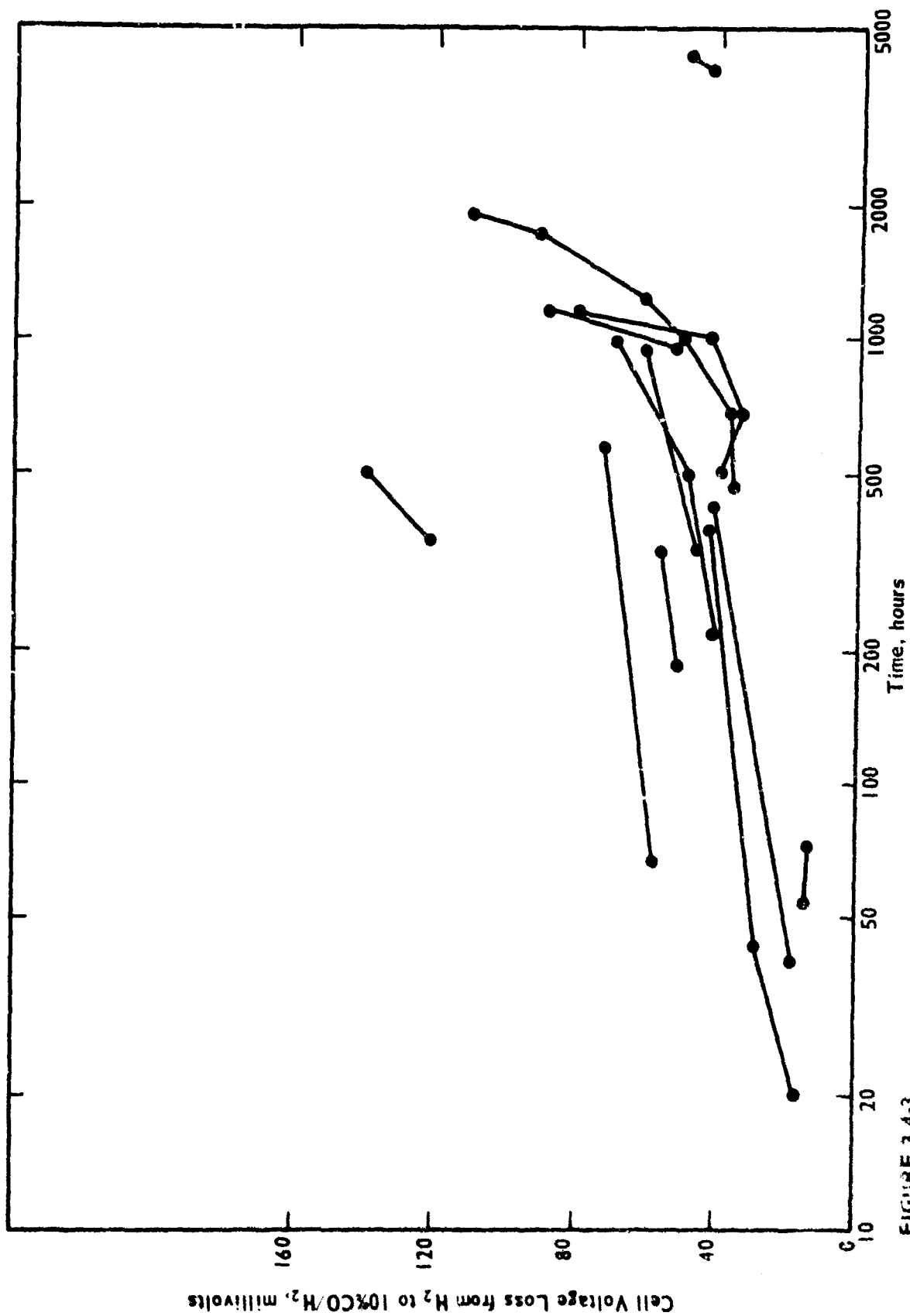Cell Voltage Loss from H$_2$ to 10%CO/H$_2$, millivolts

FIGURE 3.4-3

RA-2 ANODE LIFE TESTS:
$10\%CO/90\%H_2$ Fuel, $150°C$, $95-100\%H_3PO_4$
AA-1 and 2 Cathodes
Current Density: $100 \; ma/cm^2$
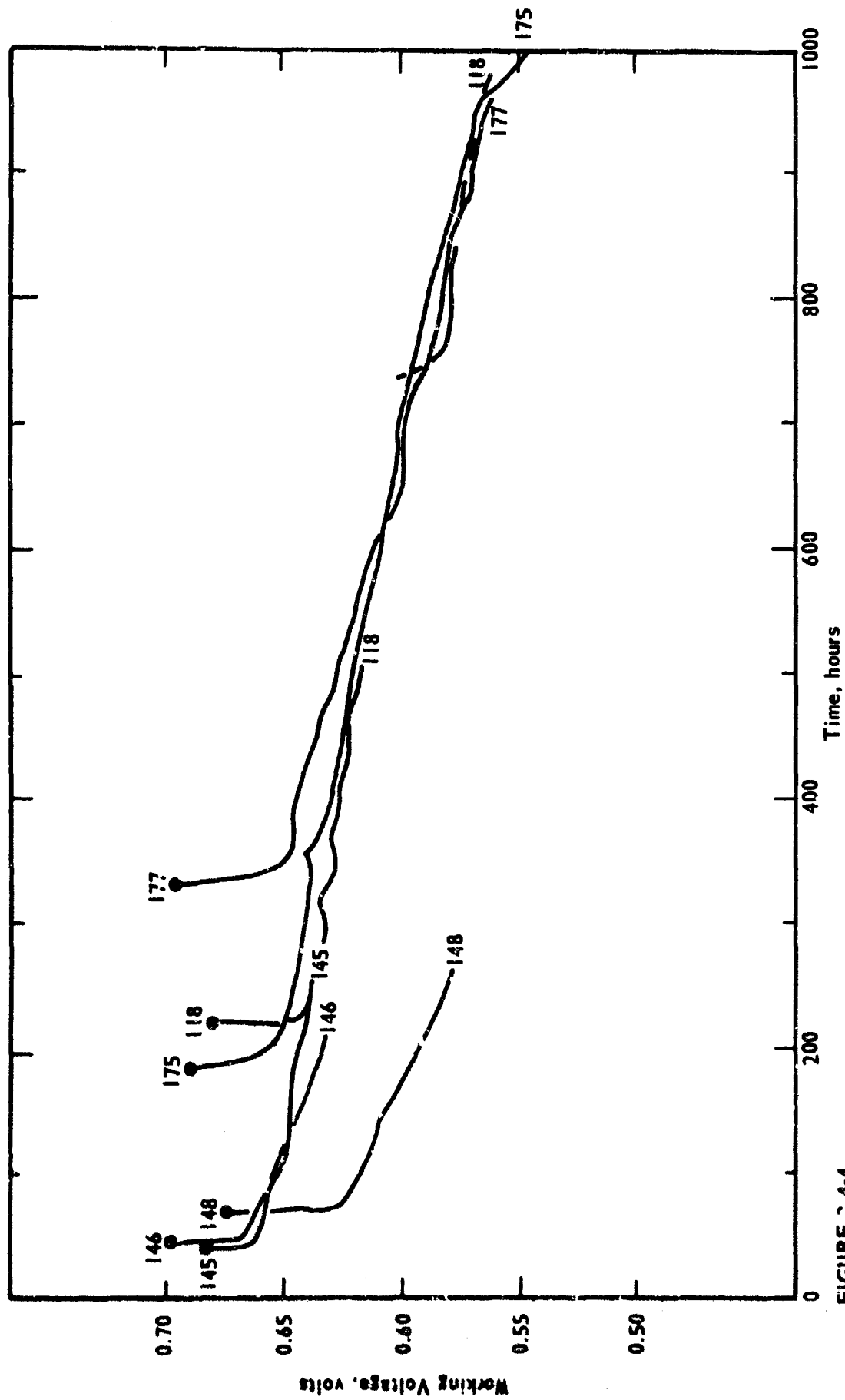
FIGURE 3.4-4

RA-2 ANODE LIFE TESTS: (No Pretreatment)
$3\%CO/27\%CO_2/70\%H_2$ Fuel, 150°C, 95-100%H_3PO_4
AA-1 and 2 Cathodes. Current Density: 100 ma/cm^2

Working Voltage, volts

Time, hours
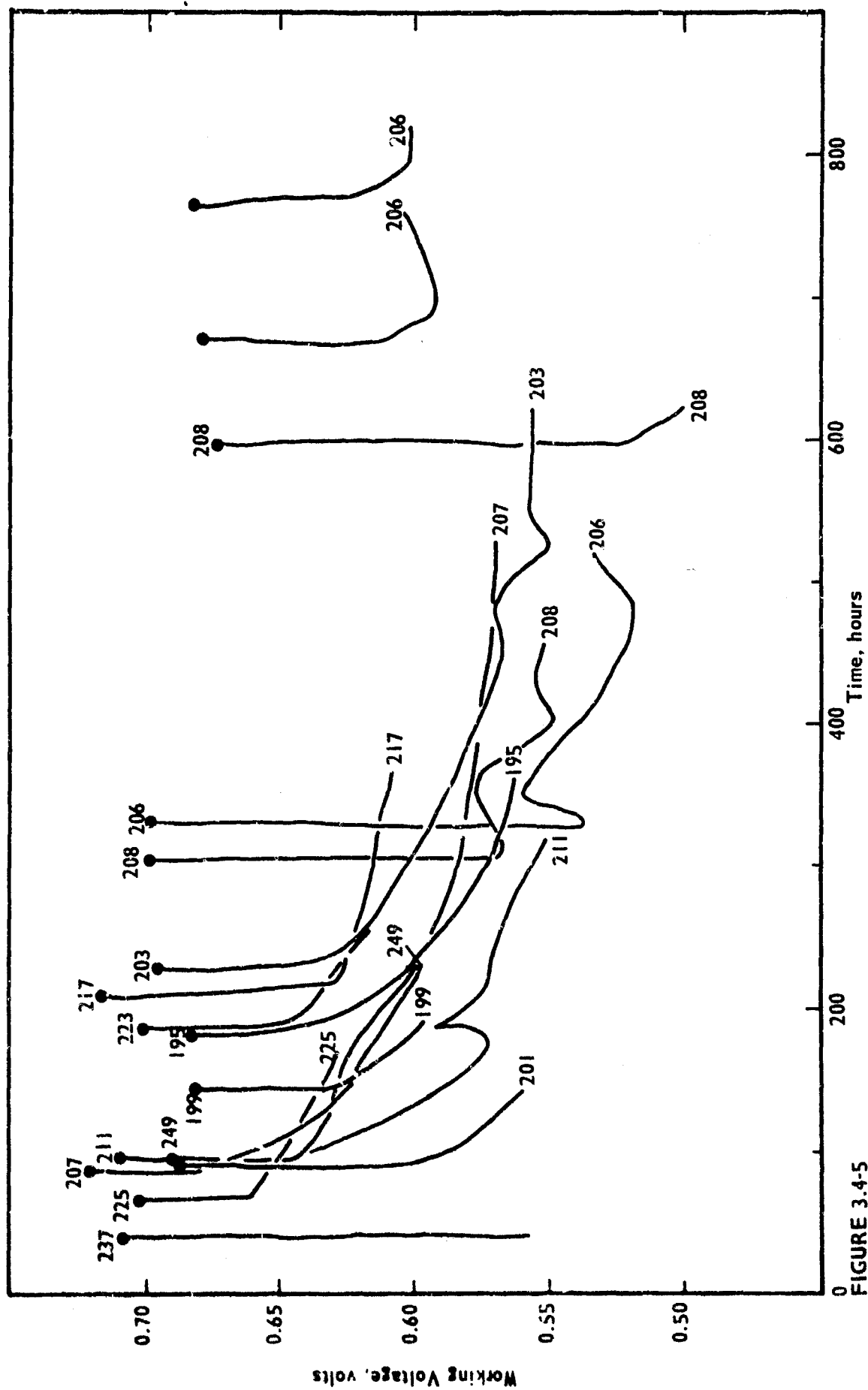
FIGURE 3.4-5

was then started in the normal manner with hydrogen at the anode and air at the cathode until a stable performance level was obtained before replacing the hydrogen with the synthetic reformate. Initial performance on the reformate was above 0.680 volt, with decline rates of 11-14 mV/ 100 hours as shown in Figure 3.4-6. The tests are shown from the point of introduction of the reformate.

At present there is no good explanation for the apparently beneficial effects of the oxygen treatment. Possibly one of the catalyst components is raised to an oxidation state which is more effective towards CO, or perhaps the treatment may remove some surface contaminant.

A "gas reversal" treatment has also been found to be beneficial if low initial performance on synthetic reformate is observed. Figure 3.4-7 shows portions of lii tests in which cells responded favorably to this type of treatment. With the exception of Test 227, these anodes had not been given an "oxygen treatment" during start-up. In the gas reversal treatment the cells were placed on open circuit, then oxygen was passed over the anode and hydrogen over the cathode for approximately ten minutes before returning the cell to operation on the reformate. Performance level and in some cases stability appear to have been improved by this treatment.

3.4.2.2 Anode Variables

3.4.2.2.1 Modified RA-2 Anodes

In the manufacture of American Cyanamid Company fuel cell electrodes, an extractable filler is normally incorporated in order to improve porosity. Modified RA-2 anodes [designated RA-2 (M)] have been made by replacing a portion of this extractable filler with a secondary

RA-2 ANODE LIFE TESTS: (O_2 Treated)
$3\%CO/27\%CO_2/70\%H_2$ Fuel, 150°C, 95-100%H_3PO_4
AA-2 Cathodes
Current Density: 100 ma/cm^2
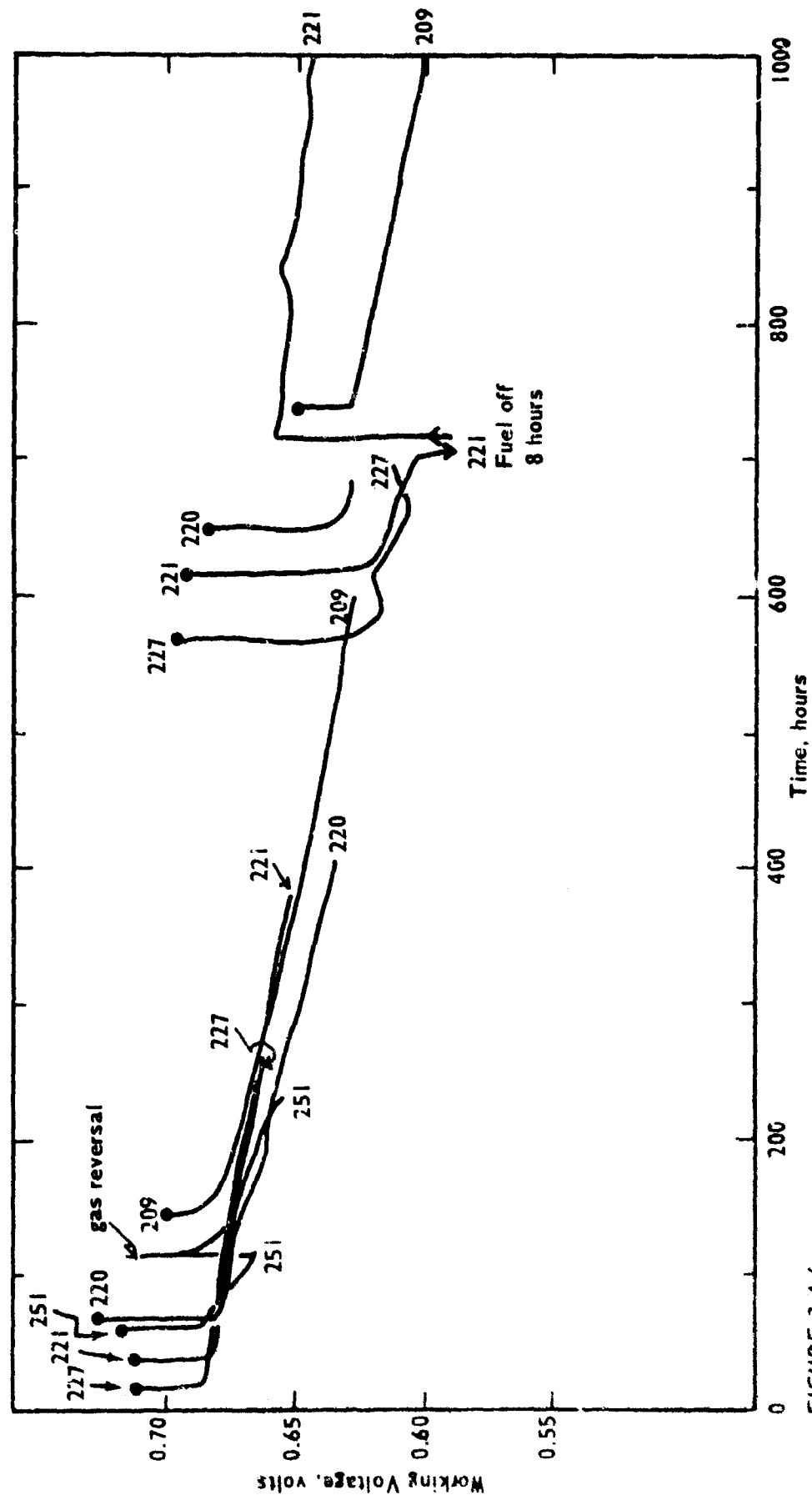
FIGURE 3.4-6

EFFECT OF GAS REVERSALS
2%CO/27%CO$_2$/70%H$_2$ Fuel, 150°C, 95-100%H$_3$PO$_4$
RA-2 Anodes, AA-7 Cathodes
Current Density: 100 ma/cm^2
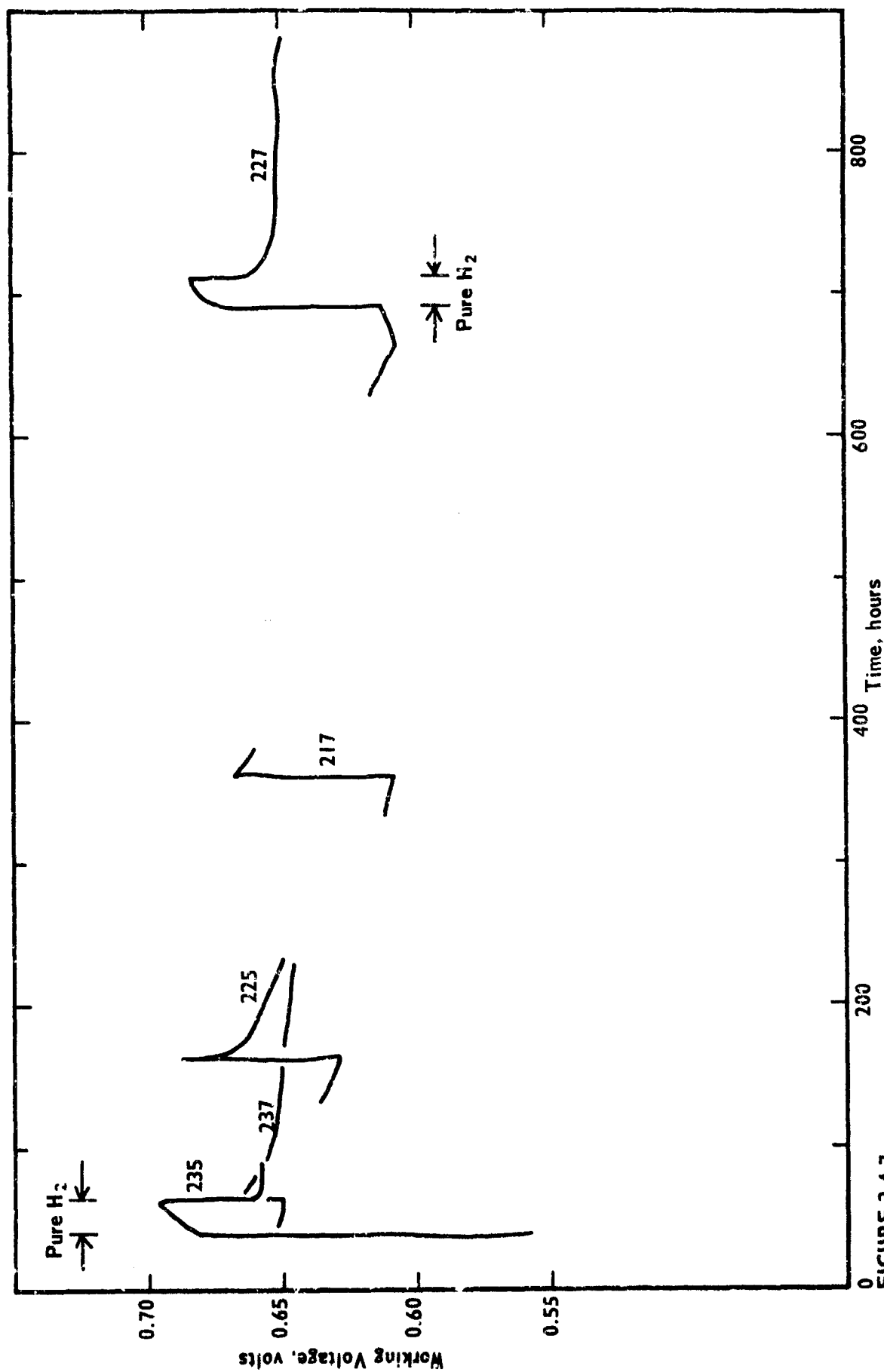
FIGURE 3.4-7

filler having a larger particle size and an elongated shape. Performance of the RA-2 (M) anodes is shown in Figure 3.4-8. Initial performance on synthetic reformate was less than 20 mV below H_2 performance; and when Test 239 was returned to pure H_2 after 820 hours of operation, the levels still differed by only 18 mV. The performance on reformate demonstrated by these cells was of the order of the best previous H_2/air values as illustrated by Test 110 in Figure 3.4-11. Further work in this area is necessary, however, since subsequent tests with electrodes from the same sheets have not performed as well.

An electrode with 5 mg/cm^2 RA catalyst but without graphite was run in Test 241, shown in Figure 3.4-9. Performance loss on switching to the synthetic reformate was high (60 mV), but there was little additional loss during the next 300 hours. The voltage decline rate thereafter appeared to be similar to that observed with RA-2 (M) anodes.

In Test 253 an RA-3 (M) electrode (3 mg noble metal/cm^2) with the modified pore structure gave a 50 mV polarization when placed on the ternary fuel mixture and showed poor stability (60 mV loss in 200 hours).

3.4.2.2.2 Type AA Anodes

The response of platinum anodes at the 5 and 10 mg/cm^2 level to synthetic reformate was determined in Tests 213 and 219, Figure 3.4-9. The AA-3 anode dropped 35 mV and the AA-2 20 mV when switched from hydrogen to the reformate. Performance level and decline rates were similar to the best results obtained with RA-2 or RA-2 (M) electrodes.

RA-2 (M) ANODE LIFE TESTS:
3% CO/27% CO_2/70% H_2 Fuel, 150°C, 95-100% H_3PO_4
AA-2 Cathodes, Current Density: 100 ma/cm²
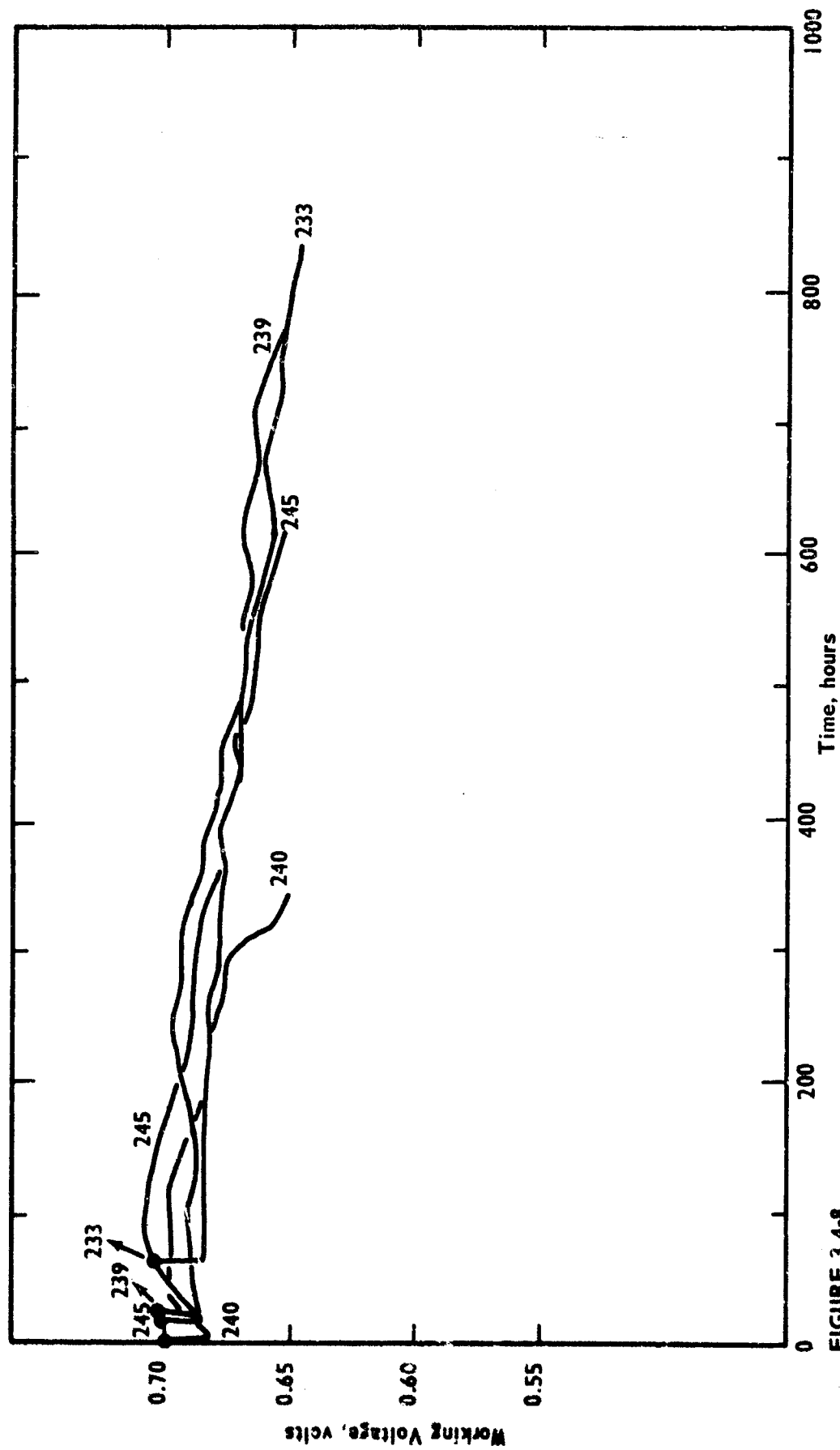
FIGURE 3.4-8

MISCELLANEOUS ANODE LIFE TESTS:
3%CO/27%CO$_2$/70%H$_2$ Fuel, 150°C, 95-100%H$_3$PO$_4$
Current Density: 100 ma/cm^2

TEST	ANODE	CATHODE
213	AA-2	AA-2
219	AA-3	AA-2
241	RA (no graphite)	AA-2(M)
253	RA-3(M)	AA-2
236	BA-5 mg Pt	BA-10 mg Pt

Working Voltage, volts

Time, hours
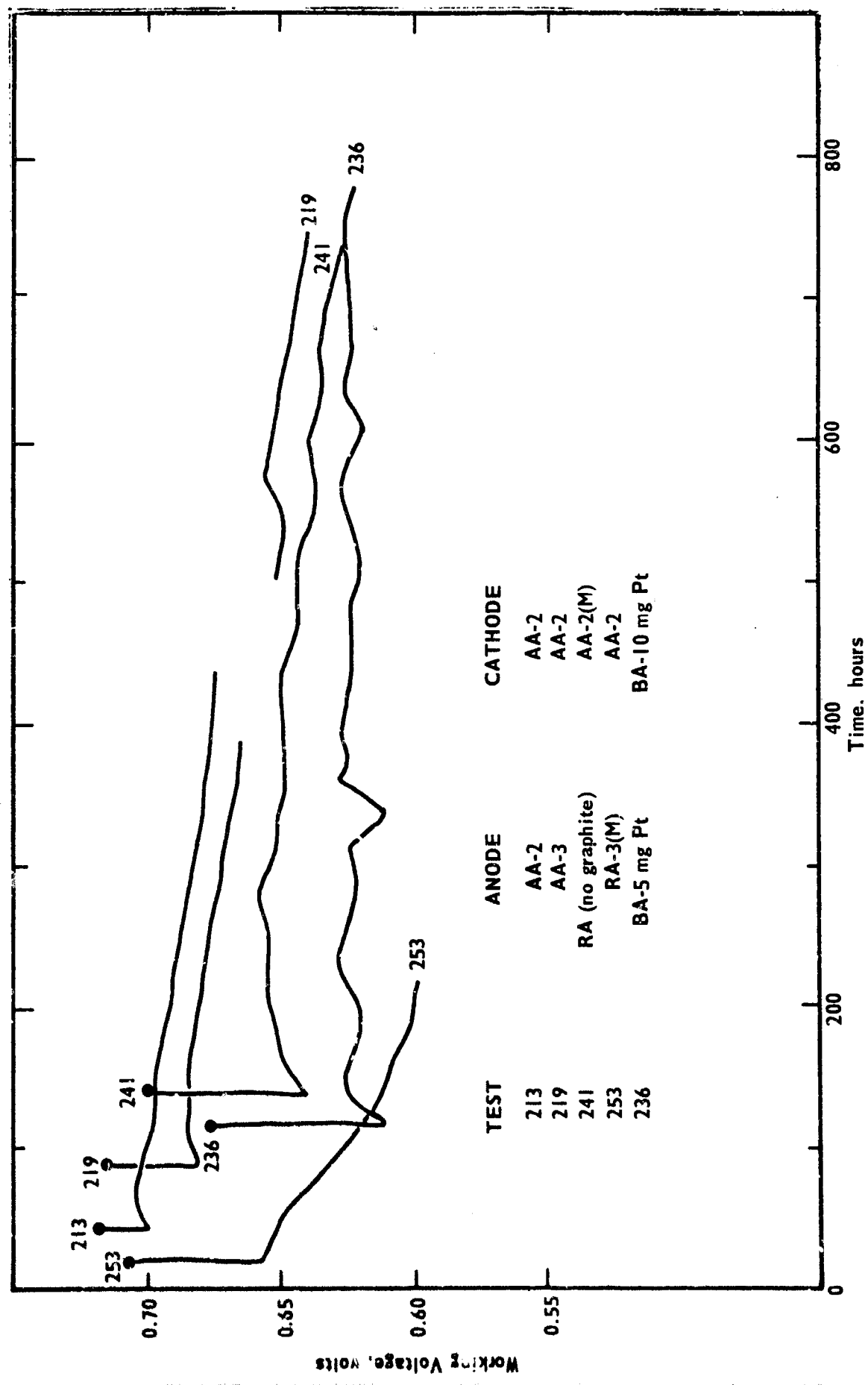
FIGURE 3.4-9

3.4.2.2.3 Type BA Anodes

Several anodes prepared from Pt, Pt-Rh, and Pt-Ru catalysts, deposited on Cyanamid graphite at 5 mg noble metal/cm^2, were evaluated on 10% CO as shown in Figure 3.4-10. All electrodes gave performance on pure hydrogen equal to a standard RA-2. The Pt-Ru and Pt-Rh anodes lost more than 200 mV on switching to 10% CO, however. The platinum anodes gave better performance on 10% CO, but voltage levels (0.55-0.62 V) were lower than have been obtained with RA-2 electrodes (Figure 3.4-4).

A platinum-on-graphite anode from the same electrode sheet used in Test 130 was also evaluated on synthetic reformate in Test 236 (Figure 3.4-9). Initial performance on H_2 was somewhat low in this test (a type BA cathode was used), and the loss in voltage on switching to reformate was greater (65 mV) than for the AA-3 electrode, which also contains 5 mg Pt/cm^2 but without graphite. The cell has operated stably on the reformate at 0.62-0.63 V for 670 hours, however, and the test is continuing.

3.4.2.3 Cathode Variables

3.4.2.3.1 Type AA Cathodes

Test 124, begun in the last report period, was set up with all noble metal screens and platinum foil lining the faceplate on the cathode side. The performance of this cell was not significantly different from cells in which the electrode support screen, backup screens, and cell plate were of tantalum (Figure 3.4-11). A repeat of this test, 155, confirmed the previous results.

TYPE BA ANODE LIFE TESTS
10% CO/90% H_2 Fuel, 150°C, 95-100% H_3PO_4
Current Density: 100 ma/cm^2

TEST	ANODE NOBLE METAL, mg/cm^2	CATHODE
130	5 Pt	AA-1
131	2.5 Pt, 2.5 Ru	AA-1
136	2.5 Pt, 2.5 Rh	AA-1
157	5 Pt	AA-2
187	2.5 Pt, 2.5 Ru	AA-2
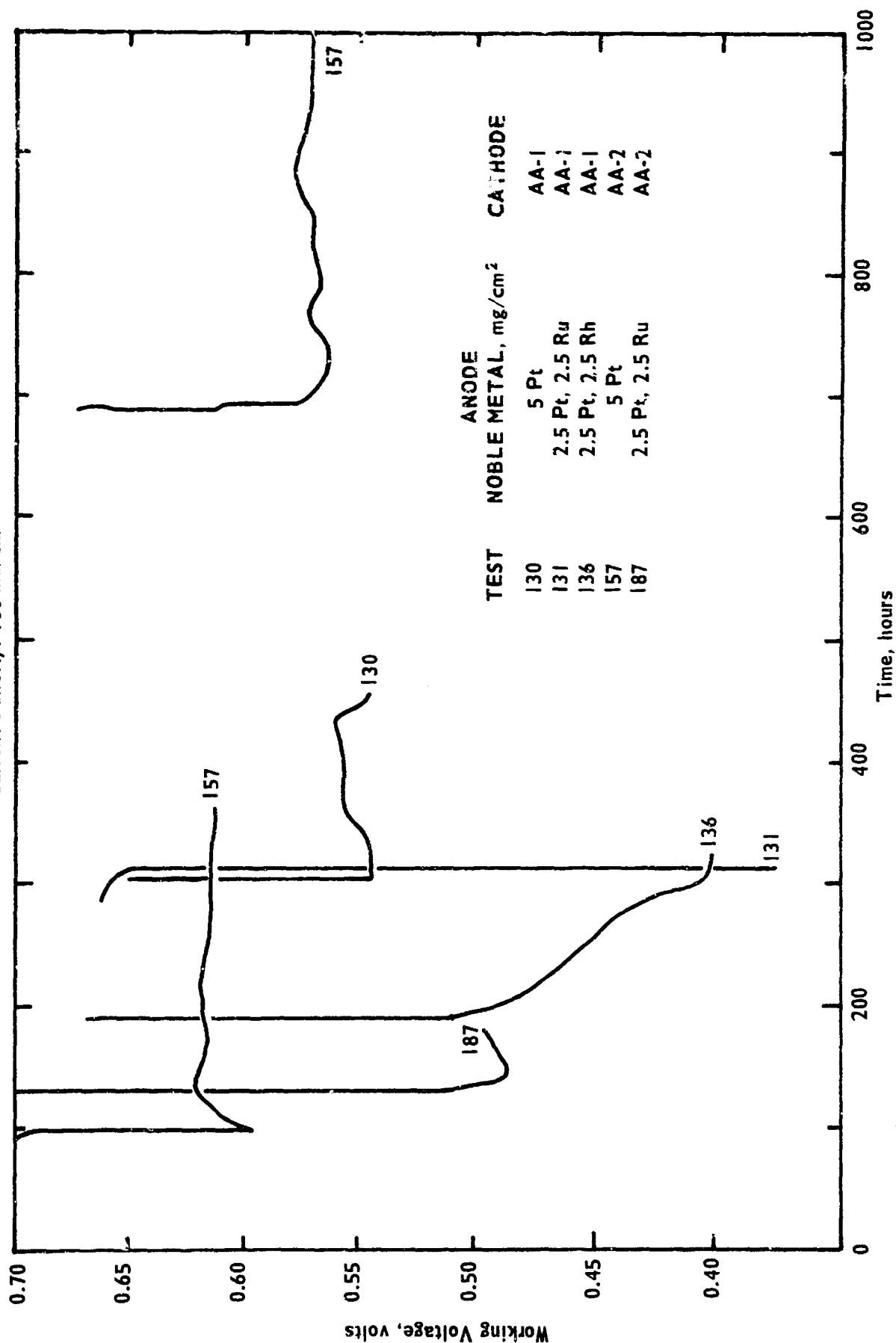
FIGURE 3.4-10

EXPERIMENTAL TYPE AA CATHODE LIFE TESTS:
H₂ Fuel, 150°C, 95-100% H₃PO₄
RA-2 Anode. Current Density: 100 ma/cm²

TEST	CATHODE	SPACER SCREENS
	AA-1	
110	AA, 10 mg Pt on Pt screen	Ta screens
124		All noble metal screens and gas chamber
154	AA-1 (extracted screen)	Ta screens
155	AA, 10 mg Pt on Pt screen	All noble metal screens and gas chamber
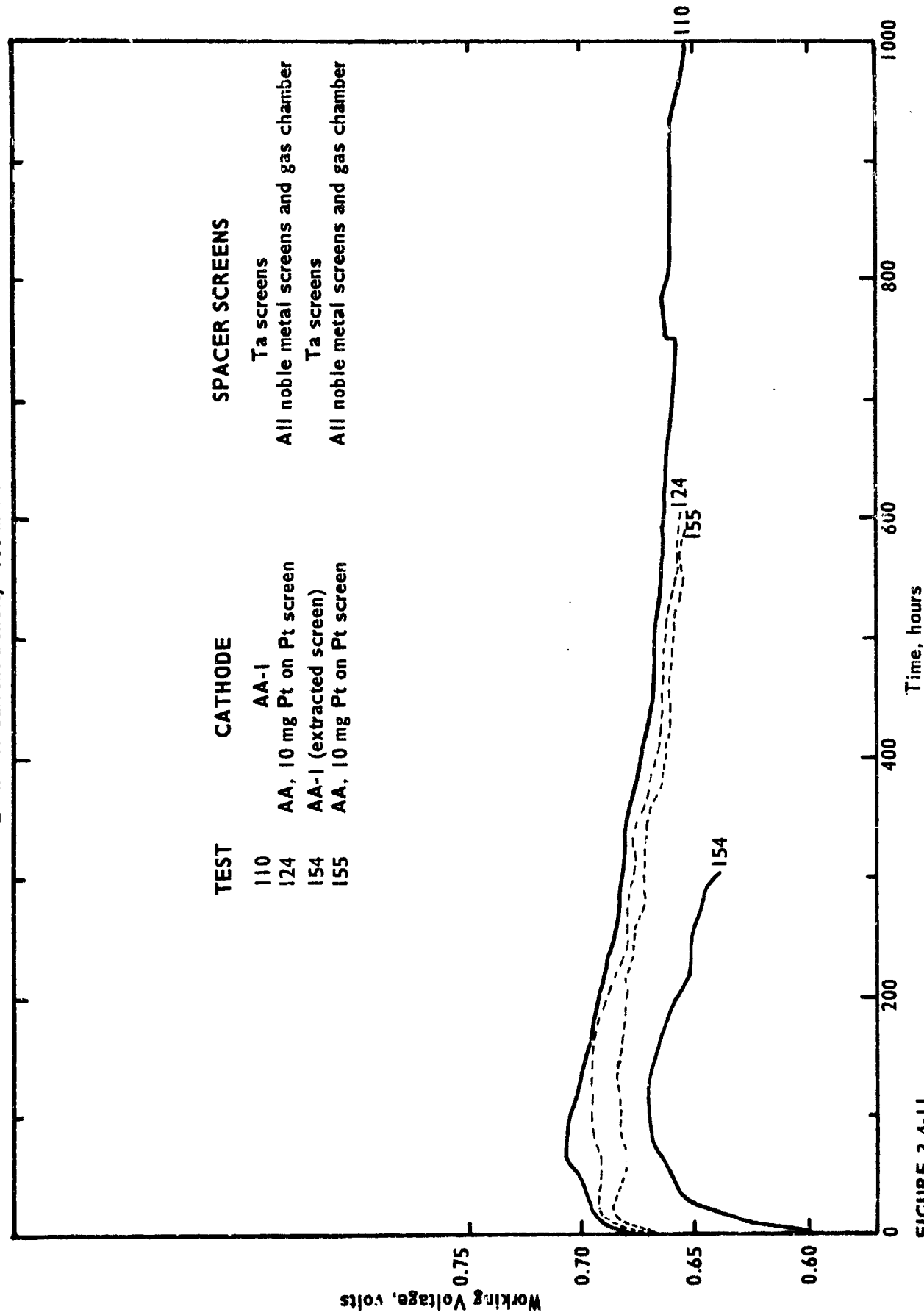
FIGURE 3.4-11

In Test 154, the cathode support screen was extracted with hydrofluoric acid, and the catalyst film pressed directly against the backup screens. This electrode structure did not perform as well as the normal screen type electrodes, and cell resistance was higher.

Cathode structure has also been varied by the addition of a secondary extractable filler as was done with the RA-2 (M) anodes. The effectiveness of this procedure is not yet clear. Cathodes of this type have given good performance in some tests and again, when paired with the same anode sheet, have performed poorly.

3.4.2.3.2 Type BA Cathodes

BA cathodes have been prepared both with Pt deposited on Cyanamid graphite and with physical mixtures of the two components at 2.5, 5, and 10 mg Pt/cm^2 loading levels. Of the higher loading group the best voltage level was obtained from a cathode in which graphite was physically mixed with platinum black (Test 144, Figure 3.4-12). Test 168 suggests that good stability may be achieved with platinum-on-graphite cathodes, although the voltage level was somewhat low (0.64 V maximum). In Test 236, Figure 3.4-9, a cathode from the same electrode sheet was used in conjunction with a type BA anode. A better level of performance was observed (0.68 V with hydrogen at the anode) and excellent stability (no voltage decline in 670 hours with synthetic reformate at the anode).

Tests with type BA cathodes containing 5 mg Pt/cm^2 are shown in Figure 3.4-13. One test with an AA-3 electrode is also shown for comparison. Test results with these cathodes were quite variable. The highest voltage (0.645 V) was obtained with an electrode in which

TYPE BA CATHODE (10 mg Pt/cm²) LIFE TESTS:
H₂ Fuel, 150°C, 95-100% H₃PO₄,
RA-2 Anode except as noted. Current Density: 100 ma-cm²

TEST	CATHODE	% PTFE
144	Physical mix, 10 mg Pt + 5 mg graphite	35
168	50% Pt on graphite	25
174	50% Pt on graphite	35
184	50% Pt on graphite	15
236	50% Pt on graphite	25
247	50% Pt on graphite	25

Working Voltage, volts

Time, hours
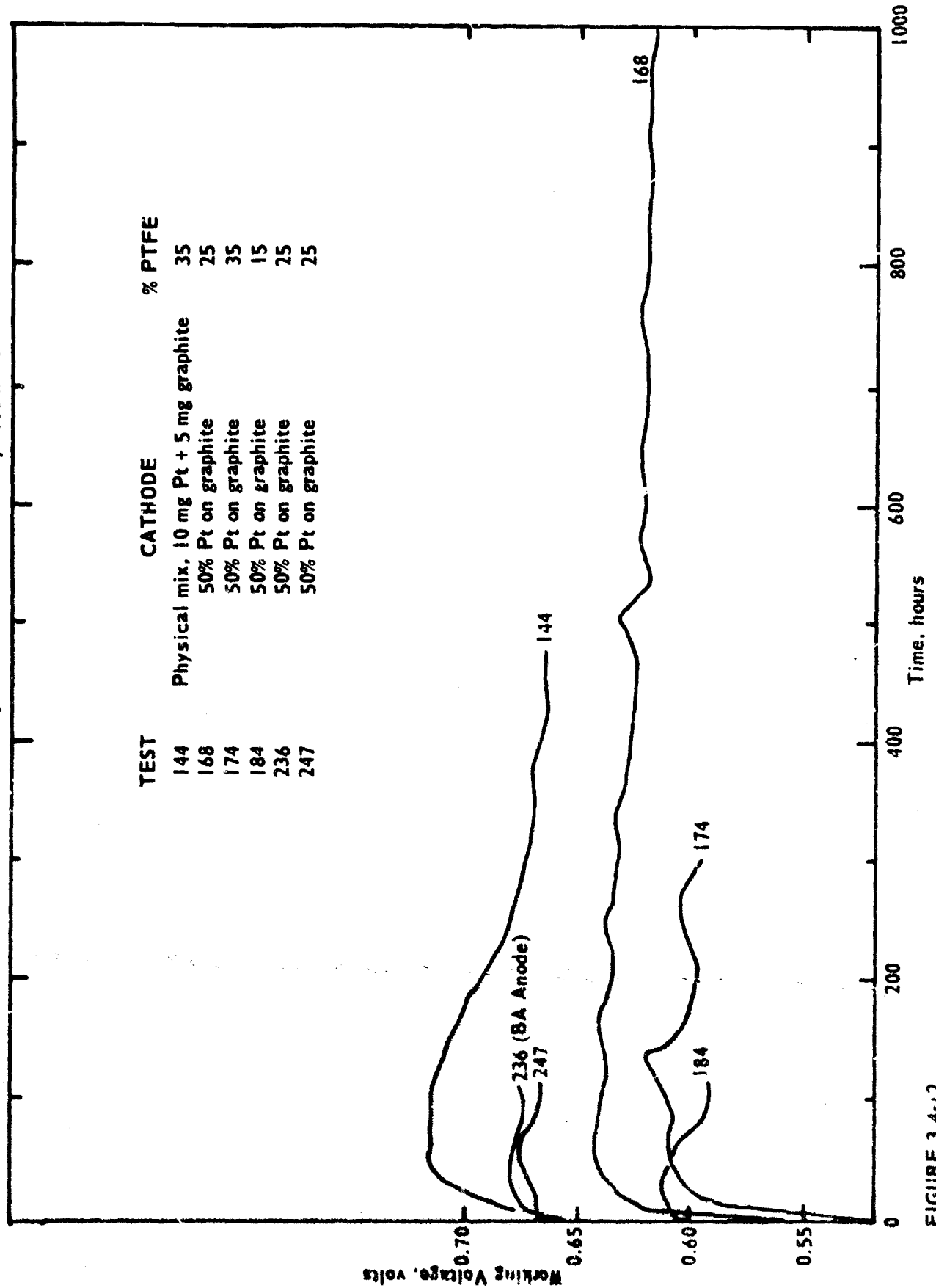
FIGURE 3.4-12

TYPE BA CATHODE (5 mg. Pt/cm²) LIFE TESTS:
H₂ Fuel, 150°C, 95-100% H₃PO₄, RA-2 Anodes
Current Density: 100 ma/cm²

TEST	CATHODE	% PTFE
134	50% Pt on graphite	25
156	50% Pt on graphite	35
180	50% Pt on graphite	25
186	50% Pt on graphite	25
257	50% Pt on graphite	35
246	Physical mix, 5 mg Pt + 5 mg graphite	35
250	Physical mix, 2.5 mg Pt + 10 mg 25% Pt on graphite	35
147	AA-3 5 mg Pt	25
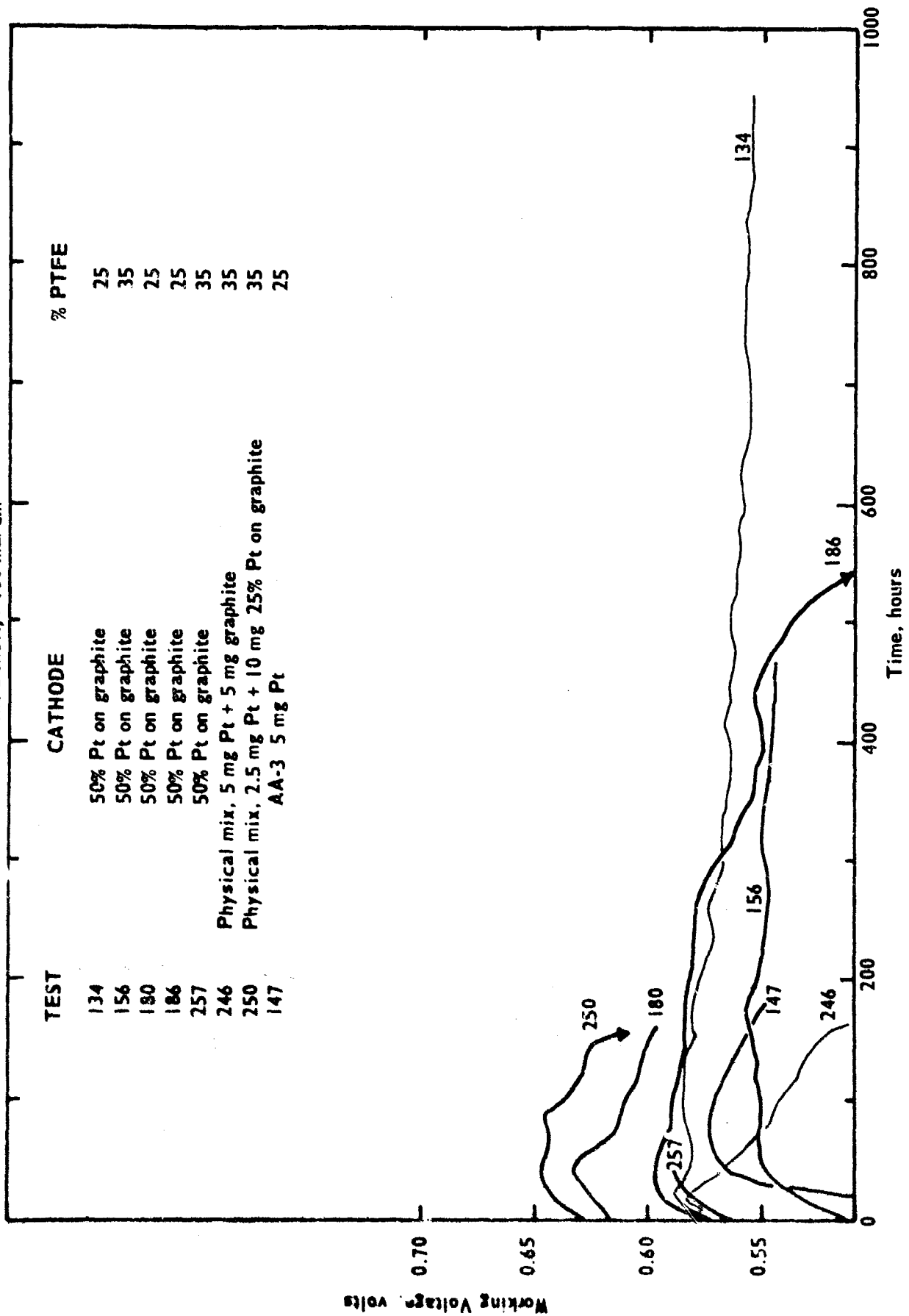
FIGURE 3.4-13

the platinum was present as a physical mixture of platinum black with platinum deposited on graphite. Again, electrodes with 50% platinum deposited on graphite (same catalyst sample as used in Tests 168 and 236, Figure 3.4-12) have given good stability (< 3 mV decline/100 hours) but at a low level of performance (0.55-0.58 V) in Tests 134 and 156.

Three tests were run with cathodes having a layered structure, with 5 mg/cm² of platinum black applied on the matrix side of the screen, and Cyanamid graphite on the gas side (Tests 152, 170, and 182, Table 3.4-1). PTFE levels were varied, but with the graphite layer always more highly waterproofed than the platinum layer. Results with this type of electrode were generally poor, the highest voltage level achieved being 0.57 V in Test 170.

3.4.2.4 Reference Electrode Measurements

A number of life test cells were set up with reference electrodes in an effort to follow individual electrode trends. The experimental set-up for the reference electrode has been previously described.[2-d] The measurements made include the IR drop through the cell, and thus are affected by changes in cell resistance. For tests in which cell resistance changes with time are small, however, the reference electrode data are felt to provide a meaningful measure of individual electrode performance. Figure 3.4-14 shows reference electrode data obtained during several tests operating for extended periods of time on synthetic reformate. The data indicate that the RA-2 anodes are reasonably stable under these conditions and that loss in cathode performance is primarily responsible for the voltage decline observed in these life tests.

LIFE TEST REFERENCE ELECTRODE MEASUREMENTS
RA-2 Anodes, RA-2 Cathodes
150°C, 95-100% H_3PO_4, Current Density: 100 ma/cm²
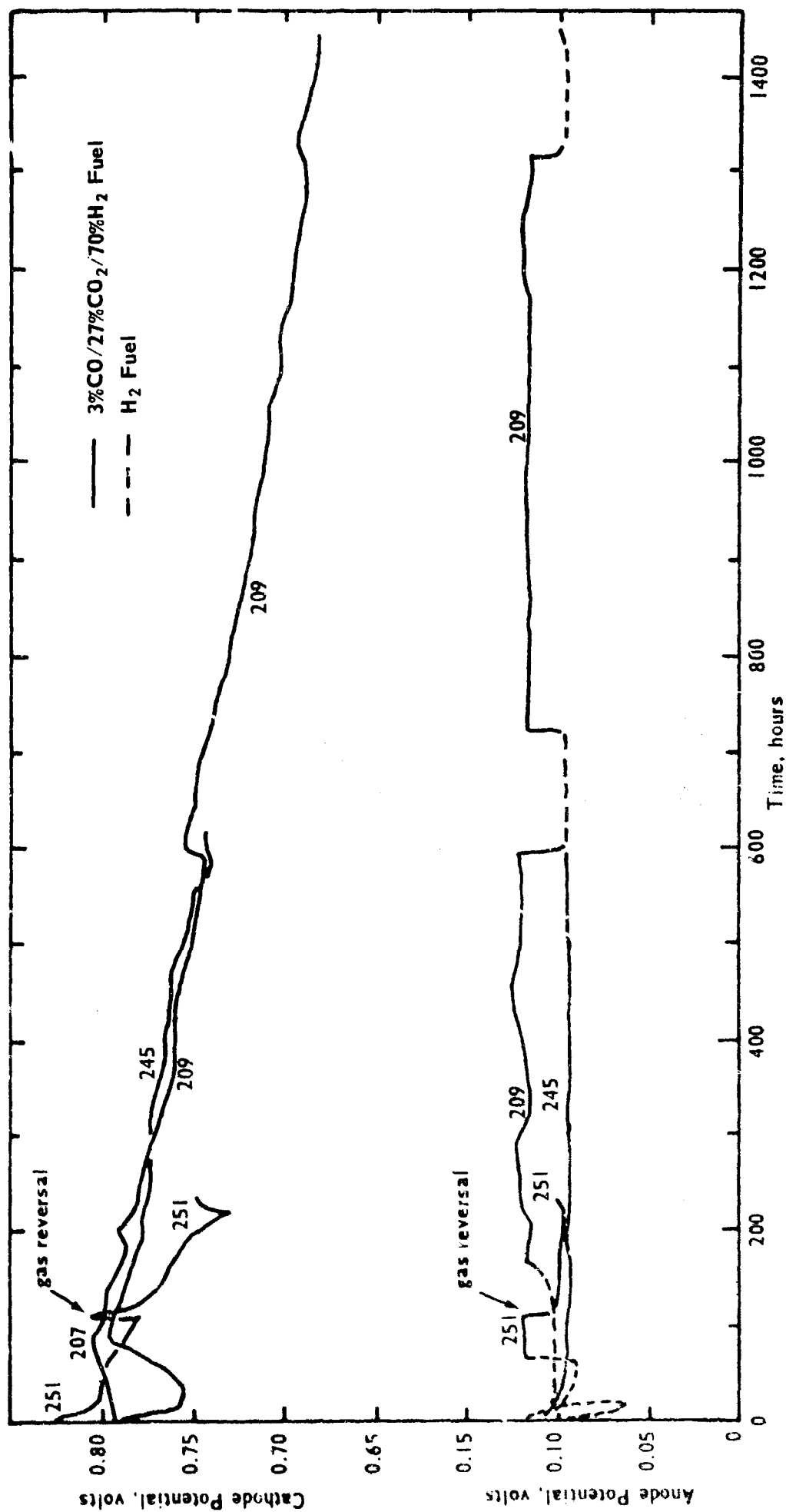
3%CO/27%CO₂/70%H₂ Fuel
H₂ Fuel

FIGURE 3.4-14

3.4.3 Tests at 100°C

Most of the life testing effort during this period was devoted to work at 150°C. However, some work has been done at 100°C with H_2, with 1%, 3%, and 10% CO/H_2 binary mixtures and with a 1% CO/29% CO_2/70% H_2 synthetic reformate.

3.4.3.1 Standard (RA-2) Anodes and (AA-2) Cathodes

The bulk of the 100°C testing has been with standard RA-2 and AA-2 electrodes. Poor reproducibility and low initial cell voltage have hampered testing in this area. Those tests which have come up to H_2/air peak voltages of 0.640-0.660 volt have exhibited excellent stability as shown in Figure 3.4-15 and also by Test 95 in Figure 3.4-2. Efforts to decrease performance variability are discussed in Section 3.4.4.

The response of RA-2 anodes to various binary CO/H_2 mixtures was obtained at intervals during the course of several life tests. The data were obtained by operating the cell with H_2/air and then switching to the impure H_2 feed and continuing operation for periods up to several hundred hours before returning to pure hydrogen. The changes in performance level were recorded for the introduction of both the impure and the pure H_2 fuel, and are tabulated in Table 3.4-4. Although the data show considerable variability between the different tests, there appears to be a general trend toward increasing response to the impure fuel with time.

Relatively stable performance on synthetic reformate (1% CO/29% CO_2/70% H_2) has been obtained in only two 100°C life tests, 198 and 214 in Figure 3.4-16. As in the previous impure hydrogen graphs, the initial point shown is the H_2/air performance prior to impure hydrogen operation. Test 198 was not stable in its initial trial on the

RA-2 ANODE LIFE TESTS
H₂ Fuel, 100°C, 85%H₃PO₄
AA-1 and 2 Cathodes, Current Density: 100 ma/cm²
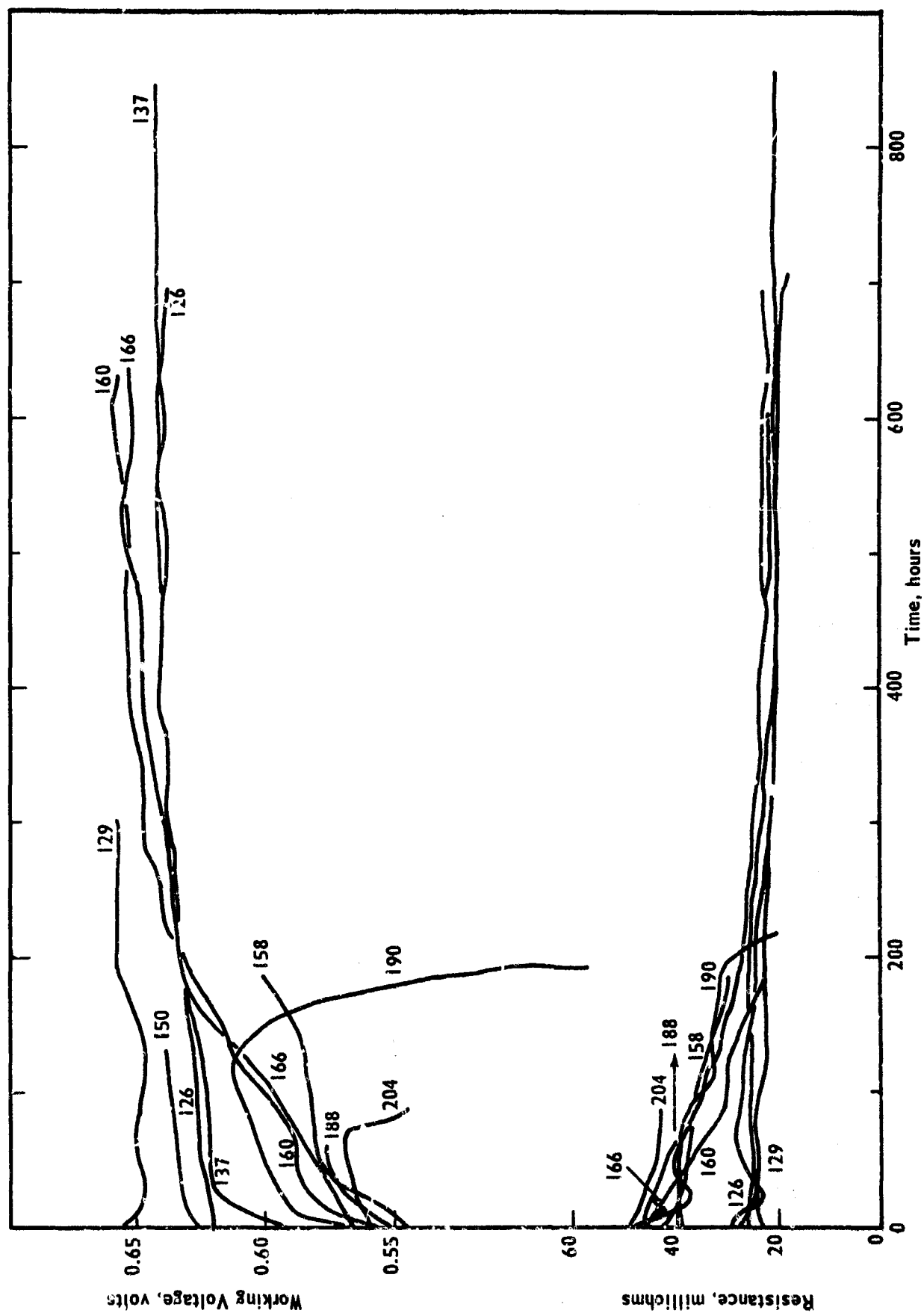
FIGURE 3.4-15

Table 3.4-4

Response of RA-2 Anodes to Various CO/H_2 Mixtures at 100°C

Life Test Number	Elapsed Time (Hours)	Change in Performance Level[1] (mV)		
		1% CO	3% CO	10% CO
108	122	32	-	-
108	258	59	-	-
108	308	-	119	-
108	594	-	159	-
108	1128	68	-	-
108	1508	129	-	-
129	880	-	21	-
129	1504	-	43	-
129	1840	-	-	76
129	2008	-	-	98
129	2490	30	-	-
129	2676	31	-	-
159	350	-	-	69
159	500	-	-	123
160	640	-	-	103
160	668	-	-	198
160	712	-	96	-
160	880	-	125	-
160	952	55	-	-

(1) Difference between voltage on pure hydrogen and that on indicated gas mixture. Current density: 100 mA/cm^2.

RA-2 ANODE LIFE TESTS:
1% CO/29% CO$_2$/70% H$_2$ Fuel, 100°C, 85% H$_3$PO$_4$
AA-2 Cathodes. Current Density: 100 ma./cm^2

FIGURE 3.4-16

- 98 -
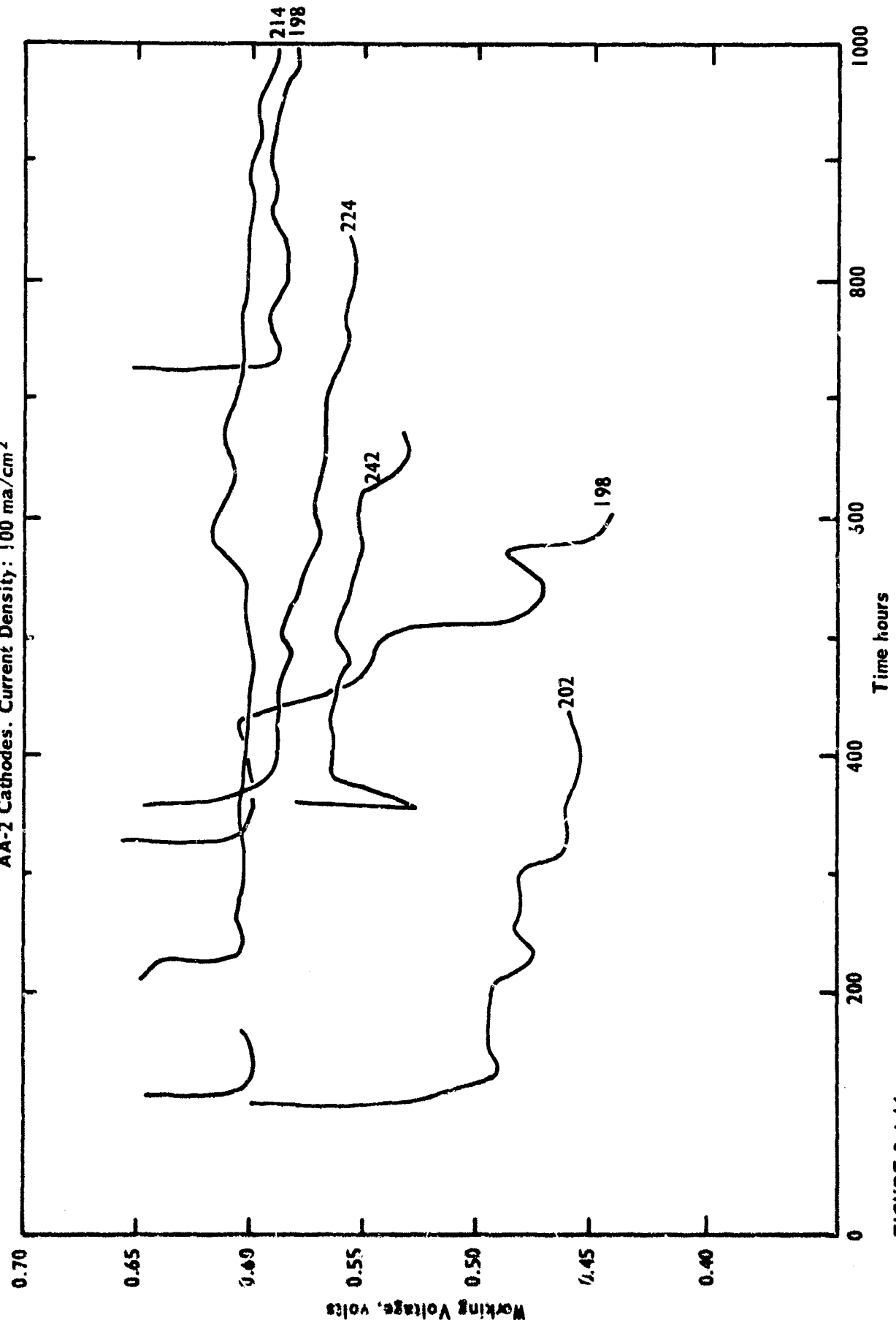
reformate but improved after a period of hydrogen operation. In Tests 202 and 242, H_2/air performance did not reach the 0.64-0.65 volt level usually expected at this temperature.

3.4.3.2 Electrode Variables

Only one test of an RA-2 (M) modified-structure anode has been made at 100°C (Test 242). Performance on H_2 was not good (0.58 V maximum), but the difference in level between pure and impure hydrogen was less than 20 mV. The pretreatment of anodes with oxygen has not been successful in 100°C testing either by treating at 100°C, or heating to 150°C, treating the anode, and then cooling to operating temperature. In both instances (Tests 228 and 232) the voltage loss on switching to synthetic reformate was 150 mV or more. These cells also contained AA-2 (M) cathodes in which the secondary extractable filler was used. Hydrogen-air performance followed the usual pattern of a slow rise to peak value.

An AA-3 anode (5 mg Pt/cm^2) gave peak H_2/air performance of only 0.610 volt in Test 226, and was unstable (would not maintain 100 mA/cm^2) on the synthetic reformate.

3.4.4 Initial Cell Performance Variability

Initial cell voltages of life tests have generally been below the peak performance values. The length of time for a cell to reach its peak voltage has varied from 0 to 180 hours at 150°C and has been as long as 400 hours at 100°C. In an effort to shorten or eliminate this start-up period, various pretreatments of electrodes, matrices, and complete cells were studied (see comments in Table 3.4-1). Electrodes and matrices were preconditioned in acid prior to assembly in cells.

Complete cell assemblies were sealed and held at operating temperature for various periods prior to start-up. Also, hydrophilic materials were "dusted" over the matrix face of the electrodes. None of these procedures had a significant effect in improving cell start-ups.

3.4.5 Crystallite Size Measurements

Crystallite size data have been obtained from several tests using type AA 10 mg Pt/cm^2 electrodes as both anode and cathode (Table 3.4-5). Cathode data are similar to that previously reported,[2-e] with a rapid early growth and then a slower continued increase. Limited anode data indicate a much slower growth rate, with only a 40 Å increase over a 9,000-hour period at 150°C and 100 mA/cm^2.

RA-2 anodes showed virtually no increase in crystallite size in tests of up to 1,200 hours at 150°C and 100 mA/cm^2. (Test 152 operated with a poor cathode and the high anode crystallite size shown is probably related to the low overall voltage.)

Data have been obtained on only a few type BA (platinum deposited on graphite) cathodes at this time, but it appears that they undergo an early rapid crystallite growth similar to unsupported platinum black.

Table 3.4-5

Crystallite Size Measurements

150°C Tests, 100 mA/cm^2

Life Test Number	Duration (Hours)	Crystallite Size (Å)	
		Anode	Cathode
AA-1 and 2 Electrodes			
116	90	122	190
80	320	140	155
85	856	125	215
165	1006	-	155
164	1300	-	160
81	9500	147	240
New AA-1 and 2 Electrodes	0	-	105-115
RA-2 Anodes			
152	18	157	-
147	184	37	-
188	620	47	-
165	1006	45	-
84	1197	47	-
New RA-2 Electrodes	0	40	-
BA Cathodes			
134	112	-	115
174	308	-	115
156	470	-	120
Catalyst[1]	0	-	65
180	188	-	155
Catalyst[2]	0	-	40

(1) Used in life test 184, 174, 156.

(2) Used in life test 180.

4. FUTURE WORK

4.1 Catalyst and Electrode Evaluation

A. Anode Catalysts

Evaluation of Pt-Rh and Pt-Ru catalysts on graphite, boron carbide, mixed chromium-tungsten oxides, and tungsten or titanium disilicide bases will be continued with the objective of determining the most practical and effective anode composition for the impure H_2/ phosphoric acid system. In particular, more effective catalysts for operation at 100°C will be sought since cathode stability appears to be much greater at 100°C than at higher temperatures. Corrosion tests on the mixed oxide and disilicide bases will be carried out in order to obtain preliminary information with respect to the utility of these materials in the hot phosphoric acid system.

B. Cathode Catalysts

Platinum deposited on various substrates by thermal reduction of platinum diammine dinitrite and by chemical methods will be evaluated alone and in admixture with platinum black. Preliminary evaluation will be on pure oxygen; the best materials will then be evaluated in electrode structures optimized for air operation.

C. Cathode Structure

Various means of modifying electrode pore structure to obtain better performance on air will be investigated. This work will include the "leached nickel foam" approach described by General Electric Company[14] as well as the use of other extractable filler materials having a favorable geometry. The effect of PTFE level and heat treatment of the electrodes (and the interactions between these variables) will be investigated.

4.2 Electro-Catalysis Studies

The work on sulfur coverage of platinum black electrodes will be extended to include other noble metal systems such as platinum-rhodium and platinum-ruthenium. Cyclic voltammetric techniques will be used in conjunction with polarization studies to investigate the functioning of these catalysts on CO-containing hydrogen fuel mixtures.

4.3 Matrix Development and Evaluation

Work with etched PTFE, tantalum pentoxide, silica fibers, and pre-digested zirconium pyrophosphate as matrix fillers will continue. A study will be made of changes in the matrix manufacturing process which together with the post-treatments described in this report may be expected to lead to matrices having improved dimensional stability without loss in porosity. In general, the objective in this phase of the program will be to develop a thinner, more porous matrix in order to reduce resistive losses in operating cells. Maintaining adequate bubble pressure in thinner matrices may be a problem. In this connection, the effect of higher PTFE levels on bubble pressure will be investigated.

4.4 Life Testing

During the next period, emphasis in the life-testing program will be placed on the evaluation of improved anode and cathode catalysts and electrode structures, as well as new matrix compositions. Initially, tests will be run to evaluate the long-term stability of various Pt-Ru catalysts received from General Electric Company. A systematic study will also be made to confirm the apparently beneficial effects of oxygen treatment and pore structure modification on the performance of RA-2 anodes noted in this report.

5. Personnel

R. G. Haldeman	Project Manager
W. P. Colman	Project Leader
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J. S. Mayell	Research Scientist
E. W. Schmitz	Scientist
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P. Firla	Scientific Assistant
D. Fletcher	Engineering Assistant

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13. ABSTRACT

This report describes the continuing evaluation of electrodes and matrix materials in fuel cell systems utilizing acid electrolytes and operating with impure hydrogen fuel.

Several experimental anodes and anode catalysts obtained from General Electric Company were evaluated in matrix cells using 5 N H_2SO_4 (70°C, 1% CO) and 85% H_3PO_4 (150°C, 10% CO) electrolytes. These materials comprised mixed noble metals (principally Pt/Ru) supported on boron carbide or a mixed boron carbide chromium-tungsten oxide substrate.

The effect of adsorbed sulfur on the performance of platinum black electrodes operating on impure hydrogen in phosphoric acid electrolyte was examined, and the stability of the sulfur-covered platinum surface with time briefly investigated.

Corrosion tests at 150°C and 200°C in 100% H_3PO_4 were run on various possible matrix filler materials, including fused quartz, zirconium pyrophosphate, and tantalum pentoxide. Matrices prepared from these materials were characterized in terms of their dimensional stability, porosity, bubble pressure, and resistivity.

Life testing in phosphoric acid cells was continued, with emphasis on characterizing the performance of standard RA-2 anodes, AA-2 cathodes, and TA-1 matrices on synthetic reformate (containing 1-3% CO, 27-29% CO_2, and 70% H_2) and air. A limited amount of testing with experimental anode and cathode structures was also carried out.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fuel cell						
Impure hydrogen						
Synthetic reformate						
Life test						
PTFE matrix						
Phosphoric acid electrolyte						
Carbon monoxide						
Boron carbide						
Sulfur						
Zirconium pyrophosphate						
Fused quartz						
Tantalum pentoxide						

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